

THE MANUFACTURE OF 1:8 AMIDONAPHTHOL
3:6 DISULPHONIC ACID H

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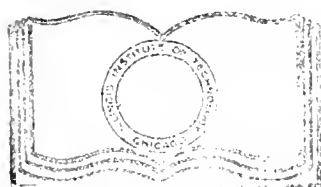
S. R. EVANS

ARMOUR INSTITUTE OF TECHNOLOGY

1922



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The manufacture of 1:8

amidonaphthol 3:6

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THE MANUFACTURE OF 1:8 AMIDONAPHTHOL 3:6 DISULPHONIC ACID H

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A THESIS

PRESENTED BY

STUART R. EVANS

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

CHEMICAL ENGINEER

JUNE 1, 1922

APPROVED:

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FOREWORD.

This thesis is respectfully submitted to The President and Faculty of the Armour Institute Technology with the object of obtaining the degree of Chemical Engineer.

It will be my endeavor to discuss in detail the entire process of manufacture of the dye intermediate product "H" acid, which process I had the opportunity of studying from the standpoint of Chief Chemist. I will endeavor to set forth the general theoretical history, together with the details of manufacture. In addition to the ordinary engineering and chemical details, I will also include a discussion of those problems that come to the attention of a chemical engineer in charge of a plant of this type, such as : the computing of plant yields and efficiencies, method of inventory, personal welfare, equipment needed, etc.

I intend, also, to include a discussion of the various methods of analysis employed in the laboratory control of manufacture and the analysis of the final product. In general, these analyses

were worked out in the plant research laboratory and were not taken from foreign literature references.

The product "H" acid is one of many dye intermediates worked out and manufactured successfully in this country by American chemists, and is but one of many proofs that America could be, if we wished to make it so, chemically independent.

This discussion is but a brief outline of the work entailed in the research of a new compound, but it includes a fairly accurate account of the details of manufacture of a plant already in steady operation and on a production basis.

"H" acid as a dye intermediate, is used in the preparation of violet to blue azo dyes. In the plant of the Newport Chemical Company it was coupled with a number of diazo compounds as follows: with para-nitraniline to form Steel Blue; with tolidine to form Diamine Blue BX and Diamine Blue 3B; with para-nitraniline to form Naphthol Blue Black; with Benzidine to form Diamine Blue 2B; with Dianisidine to form Diamine Sky Blue; and

with ortho toluidine to form Fast Acid Fuchsine.

"H" acid when manufactured as the dye intermediate is seldom isolated as the pure Amidonaphthol disulphonic compound, but is produced commercially as the acid sodium salt. This acid sodium salt forms white needles which are slightly soluble in water but readily soluble in sodium carbonate solution. The acid sodium salt crystallizes with one and one-half molecules of water of crystallization.

"H" acid (sodium salt) forms a yellow solution with diazo compounds and a brown red color with ferric chloride.

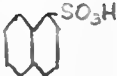

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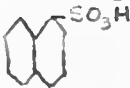
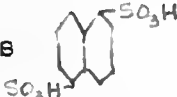
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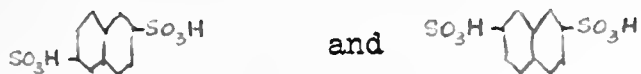
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DISCUSSION OF THE VARIOUS NAPHTHALENE
TRISULPHONIC ACIDS LEADING TO THE MAN-
UFACTURE OF "H" ACID.

When Naphthalene is heated with strong sulphuric acid, both the alpha and beta-Naphthalene monosulphonic acids are formed in varying quantities according to the temperature of the reaction. According to the law discovered by Armstrong and Wynne, the sulphonic acid group enters the alpha position at low temperatures and the beta position at high temperatures . On treating Naphthalene with very strong sulphuric acid at 80 degrees C., a-Naphthalene sulphonic acid  is produced; while at 180 degrees C., b-Naphthalene sulphonic acid is the chief product .

The same law holds for further sulphonation. The second sulphonic acid group enters the most remote a-position at low temperature, and the most remote b-position at high temperatures. On further sulphonation in the cold, the a-sulphonic acid  forms  as the chief product, and at higher temperatures the sulphonic acid

while the b-sulphonic acid forms, on further sulphonation at 160 degrees C., the sulphonic groups in positions 2:6 and 2:7 as chief products,



Thus, in the formation of the Naphthalene sulphonic acid for "H" acid manufacture the question of plant control is very important in order to guide the sulphonic acid groups to their correct positions, forming the sulphonic acid combination that will eventually lend to the correct Amidonaphthol disulphonic acid. To this end the following theoretical steps are necessary:-

- 1- Naphthalene and sulphuric acid at 180 degrees C. forms,
 - a- Naphthalene sulphonic acid.
- 2- Further sulphonation with strong sulphuric acid in the cold (95 degrees C.) forms
 - 1:6 b- a- Naphthalene disulphonic acid.
- 3- Final sulphonation at 160 degrees C. forms
 - 1:3:6 b- a- b- Naphthalene trisulphonic acid.

It is of utmost importance that these various steps in the process be carefully watched, and the specifications for time and temperature control

carefully executed, in order to bring about the right combination of sulphonic acid groups, otherwise the final reactions may lead to any one, or a mixture of a dozen or more, Amido-naphthol sulphonic acids.

DISCUSSION OF VARIOUS METHODS OF
MANUFACTURE OF "H" ACID.

The best method for the manufacture of "H" acid is that which requires only ordinary available chemicals and which does not tax the knowledge of the average plant workman, making necessary too much expert supervision.

"H" acid can be produced in a number of ways, two of the most important of which are as follows:-

- A- (a) The sulphonation of Naphthalene to
1:3:6 Naphthalene trisulphonic acid.
- (b) Nitration of the 1:3:6 body to 1: Nitro-
naphthalene 3:6:8 trisulphonic acid.
- (c) Reduction of the 1: nitro-3:6:8 body to
1:amino 3:6:8 trisulphonic acid.
- (d) Fusion of the Amino body to 1: Amino-
8: oxynaphthalene (or naphthol) 3:6
disulphonic acid "H".
- B- (a) The sulphonation of Naphthalene to
2:7 Naphthalene disulphonic acid.
- (b) Nitration of the 2:7 body to 1:8 dinito-
naphthalene 3:6 disulphonic acid.

(c) Reduction of the 1:8 dinitro 3:6 di-sulphonic body to 1:8 diamido naphthalene 3:6 disulphonic acid.

(d) Conversion of the diamido body to 1:8 Amido naphthol 3:6 disulphonic acid "H".

In method "B", the basic product generally used is 2:7 Naphthalene disulphonic acid. This may be obtained through direct sulphonation of Naphthalene or from b-naphthalene monosulphonic acid. It is rarely obtained as a uniform product but usually contains large percentages of 2:6 Naphthalene disulphonic acid; if formed from the b-monosulphonic body; and if formed from Naphthalene it contains disulphonic acids of the 2:6, 1:6 and 1:5 series. These other acids do not form "H" acid. In order to form a fairly pure basis for the Amido naphthol, it would be necessary to make a separation of the 2:7 disulphonic acid from the acids of other series. This is almost impossible; at least it would make the cost of manufacture prohibitive.

Another reason which renders method "B" unfavorable, is the necessity of too much special

apparatus. The conversion and separation of the various disulphonic acids requires special apparatus. This also holds true for the conversion of diamino-disulphonic acid into azimido-alpha disulphonic acid (with sodium nitrite) and its decomposition in an acid solution, whereby through coupling, a certain amount of dyestuff is formed. This process, according to old patent literature, works very well in the laboratory, but is not a practical plant process.

This leaves method "A" as the best method available and it was this method that was used successfully during the period that I worked as Chief Chemist in the "H" acid division.

There are a number of difficulties contingent upon successful operation of an "H" acid plant. Amongst these are:-

- (a) The production of a uniform Naphthalene 1:3:6 trisulphonic acid.
- (b) The quantitative working up of the Amino body.
- (c) The quantitative fusion of the Amino salt while avoiding the formation of other fusion products.

Naphthalene 1:3:6 trisulphonic acid can be produced in two ways, either by direct sulphonation of Naphthalene or through the sulphonation of b-Naphthalene monosulphonic acid to 1:6 disulphonic acid, which as well as 2:7 disulphonic acid, forms 1:3:6 trisulphonic acid.

The sulphonation is carried on so that only 1:6 disulphonic acid results as an intermediate product. On a laboratory experimental scale this can be carried on very smoothly, but in the large plant sulphonators it is impossible to form only 1:6 disulphonic acid. With careless supervision, a variance of time and temperature control will give a large quantity of other disulphonic acids, both of which form trisulphonic acids that will not form "H" acid.

(a) 1:5 Disulphonic acid \rightarrow 1:3:5 trisulphonic acid \rightarrow

1:8 Amido naphthol 4:6 disulphonic acid.

(b) 2:6 Disulphonic acid \rightarrow 1:3:7 trisulphonic acid \rightarrow

1:5 Amidonaphthol - 3:7 disulphonic acid.

In addition to these, tetra sulphonic acids are formed, which on fusing, form oxy- and dioxy-sulphonic



acids. All these products are harmful to the production of "H" acid, as in the later formation of dyes from this intermediate, they exert a color changing influence. Instead of a clear sky-blue shade, they will form dyes with a reddish or brownish cast.

The entrance of the three Sulphonic acid groups into the Naphthalene ring is carried out in three distinct successive steps in one sulphonator. According to some of the methods employed in the patent literature, a sulphonation of the Naphthalene to the beta-mono-body is first affected, this body separated out as the sodium salt, and the entrance of the remaining sulphonic groups carried out in subsequent sulphonation.

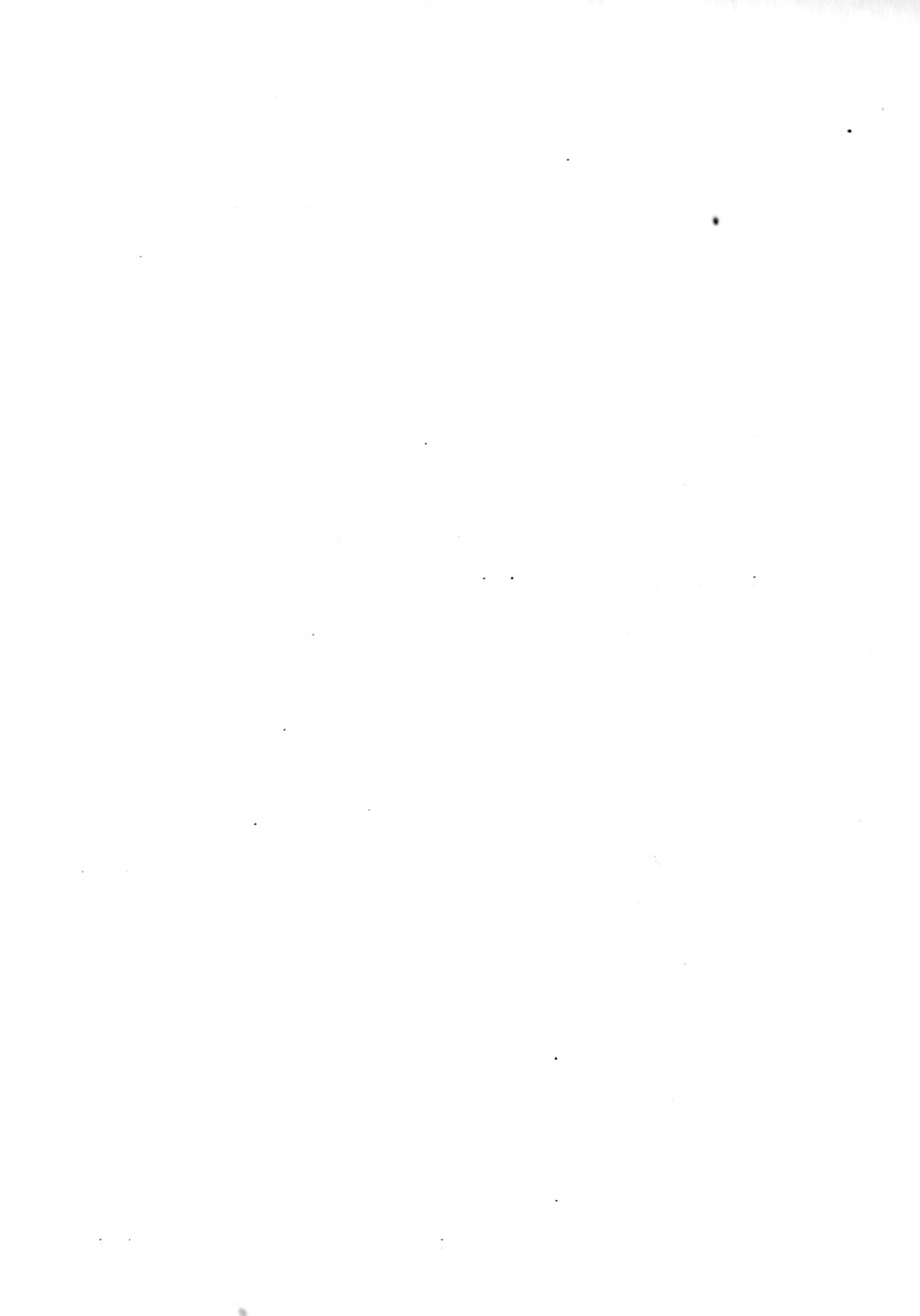
The method worked out in the laboratory and plant of the Newport Company seemed far more efficient and led the way to greater production. Unless the "1:3:6" process is carried out with strict adherence to temperature and time control, and strength of the raw basic materials, it will lead to the formation of a number of harmful by-products. The first step, the formation of the b-mono-sulphonic acid in the sulphonator, is affected

with 18% Oleum. Stronger Oleum than this is not desirable from a manufacturing viewpoint because the temperature cannot be controlled as well. Slight deviations in the duration of the reaction or in the temperature, through negligence of the operator are not of such great consequence when the weaker Oleum is used.

Even with the use of 18% Oleum, unless time and temperature are adhered to, the undesirable 2:6 disulphonic, 1:3:7 trisulphonic, and the tetra sulphonic acids will occur.

A number of other conditions may arise to cause the formation of by-products. A condition established for one production in one type of sulphonator cannot be applied to all. Slight changes in the apparatus, methods of adding acid, methods of cooling and heating, of temperature control, and above all, inefficient stirring of the contents, cause the formation of undesirable sulphonic acids.

Excessive sulphonation should also be avoided, inasmuch, as this leads to the formation of tetra sulphonic acids. It is better to have some of the under-sulphonated 1:6 body in the final 1:3:6



trisulphonic acid, than to have the tetra sulphonic acid, as the 1:8 Amidonaphthol 3:sulphonic acid, which results from the 1:6 disulphonic acid is more closely related to "H" acid than the naphthol-sulphonic acids which form from the tetra bodies. That is, the dyes from the 1:6 acid have approximately the same color as those formed from "H" acid and appear less unfavorable than the dyes from the tetra acids.

THE PROCESS.

SULPHONATION OF NAPHTHALENE TO 1:3:6

NAPHTHALENE TRISULPHONIC ACID.

The sulphonation is carried on in the usual type of cast iron, unjacketed sulphonator with a capacity of from 400 gallons to 800 gallons, depending upon the charge of Naphthalene used. For a 350 pound charge of Naphthalene, a sulphonator with a capacity of 400 gallons is sufficient. The sulphonator is provided with cast-iron water cooling sections, approximately 4" in diameter, suspended from the cast iron cover and extending to within about 12" from the bottom. About eight sections are necessary for a 400 gallon sulphonator. A double-propeller type of mechanical stirring device is provided, the propellers so placed that one is at the bottom of the suspended shaft, and the other^{placed so} that it revolves in the upper half of the contents of the kettle. The propellers are placed so their stirring action is reversed, and the bottom one causing a whirling action upward, the upper one causing a downward motion. A #210 Tycos recording thermometer, the extension bulb of which

is placed in a tube suspended in the kettle, is used to record the temperature of the contents. This thermometer tube is filled with a high-flash cylinder oil which renders the taking of a uniform temperature. The sulphonator is provided with a radial type of gas burner with air and gas connections for blast heating. The contents of the sulphonator may be blown out by means of high pressure compressed air through an outlet tube which extends from the bottom of the inside of the kettle, out through the top and over to the nitrators.

A vent pipe, two inches in diameter, extends from the top of the kettle up through the roof of the plant. Draught is induced by means of a steam vent so arranged that condensing vapors do not drop back into the sulphonator, but are trapped and allowed to flow to the sewer. The draught induced in the vent also causes Naphthalene vapors to ascend with the acid fumes. This loss of Naphthalene may be prevented by regulating the steam draught at the beginning of the sulphonation, before the Naphthalene has been completely taken up by the acid. Even with

the exercising of all precautions some Naphthalene escapes. A large portion of the escaping Naphthalene sublimes in the vent pipe about three to five feet above the sulphonating kettle. To prevent the clogging of the vent, and in a measure to return some of the sublimed Naphthalene to the kettle, the vent pipe is wound for a distance of about five feet with $\frac{1}{4}$ inch lead tubing, and through which low pressure steam is passed. One would think that this warming of the vent would aid in the vaporizing and subsequent loss of Naphthalene. Such is not the case inasmuch as the Naphthalene seems to pass through a stage of sublimation and then melting and dropping back into the sulphonator, instead of remaining in the vapor stage and being lost through the vent.

The vent pipe is adjustable so that it may be raised when the contents of the kettle ~~are~~ ready to be blown out, thus making it possible to close the vent opening in the cover, rendering the kettle air-tight.

I will take for the discussion of the operation the quantities of raw material equivalent to a

350 lb. charge of Naphthalene and will compute
all plant data and efficiencies from this charge.

THE SULPHONATION.

With the agitator on the idler pulley, 350 lbs. of Naphthlene (M.P. 79.8 degrees C.) is accurately weighed and shoveled through a charging hole in the top of the sulphonator, after the operator has convinced himself that the vent pipe has been thoroughly steamed out and all water blown from the cooling sections. The cover is clamped over the charging hole, the gas burner lighted, and the Naphthlene is heated slowly to 160 degrees C. The heating is regulated so that 160 degrees is reached in about forty minutes. In order to prevent overheating at the start, it is best to shut off the gas burner when the temperature reaches 125 degrees C., allowing the heat retained by the kettle to continue the rise to 160 degrees.

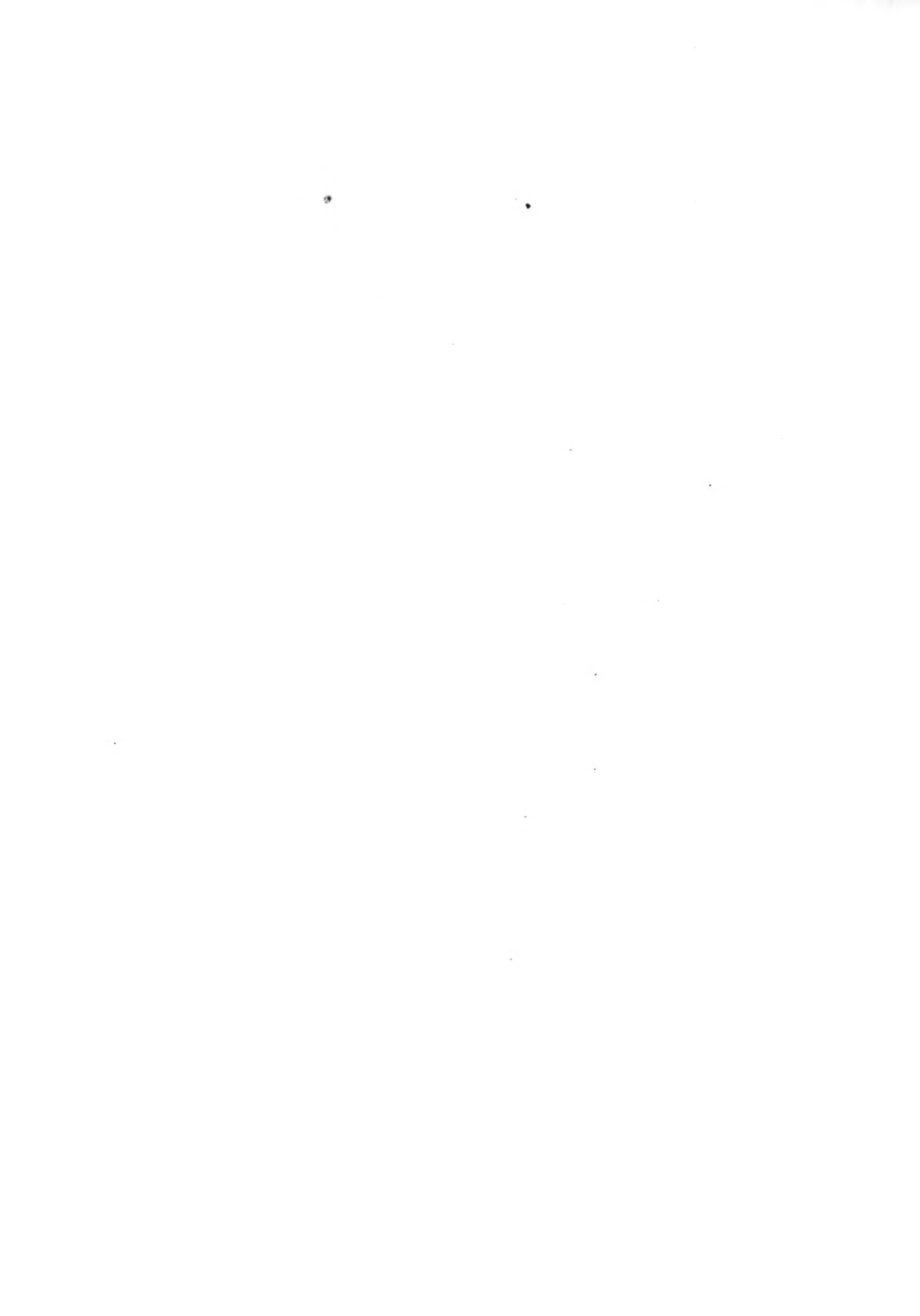
Inasmuch as the exchange of heat between the contents of the kettle and the oil in the recording tube is not instantaneous, and allowance of 10 degrees is made, so that all apparent temperatures noted in the discussion will be about 10 degrees lower than the actual or true temperatures.

When the temperature of the Naphthalene reaches 160 degrees and starts to recede slightly, conditions are right for the addition of the 18% Oleum to form the beta-mono sulphonic acid. Acid is never added to the Naphthalene while the temperature is rising, inasmuch as the reaction is apt to get beyond the control of the operator. 18% Oleum is now allowed to run in a slow stream into the sulphonators from a storage tank placed on a platform or floor above. The lines from the Oleum storage tanks are of lead with a sight glass placed in the line above the kettle to enable the operator to watch the flow. Operators are not as a rule informed of the weight of Oleum necessary for the sulphonation, but are given their orders in terms of inches of Oleum measured in the storage tank. 490 lbs. of 18% Oleum are necessary for the first step in the sulphonation.

The addition of 18% Oleum consumes from forty-five minutes to an hour. If the reaction becomes too violent and the temperature rises above 165 degrees C., the contents may be cooled slightly by

turning on the compressed air through the gas burner. If this fails to check the rise in temperature, the cooling sections may be filled with water for a few minutes, or until the reaction is under control. After the reaction has subsided all water is blown from the cooling sections and the remainder of the 18% Oleum added. After half of the acid has been added, the reaction is much less violent and it may be necessary to heat the contents by means of the gas burner in order to hold the temperature at 165 degrees C. Immediately after all the 18% Oleum has been added, the mass is heated to 170 degrees C.(inside) and held at that temperature for one hour. With good control of temperature a good formation of the beta-mono sulphonic body should result, with very small percentages of by-products.

To prepare for the entrance of the second sulphonic acid group, the formation of beta-alpha-disulphonic acid, the temperature of the contents is brought down to 95 degrees by blowing air up through the fire box and by passing water through the cooling tubes. It usually takes from three to four hours to cool the sulphonation to this temperature.



Keeping the temperature between 90 degrees and 100 degrees C., 2450 lbs. of 25% Oleum is added from the storage tank. During the addition of the first half of the Oleum, water is passed through the cooling tubes to curb the reaction; after this, the tubes are emptied by air pressure and the sulphonation heated to prevent the lowering of the temperature. The addition of 25% Oleum requires about two hours, after which the temperature is held constant at 95 degrees to 100 degrees C. for two hours.

The sulphonation is now ready for the third sulphonic acid group, the beta-alpha-beta body, or 1:3:6 Naphthalene trisulphonic acid. This is carried on without the further addition of acid, inasmuch as the excess of acid in the sulphonator is sufficient to force the third sulphonic acid group into position at a high temperature. Consequently, the temperature is raised by gas heating to 165 degrees C. within one to one and one half hours and held at 165 degrees for six hours. The control of temperature at 165 degrees is affected by air-cooling the bottom of the sulphonator or,

in case of a drop in temperature near the end of the six hour period, by heating slightly. The finished sulphonation, as 1:3:6 Naphthalene tri-sulphonic acid is now cooled by passing water through the cooling tubes, to about 125 degrees C.

The vent connections to the sulphonator are now taken off, the cover clamped into position and the sulphonation mass blown by high pressure air through the delivery line to the nitrator. The sulphonator vent is now thoroughly steamed out, all water blown from the cooling sections and everything is in readiness for another sulphonation.

* For schedule of plant operations see page 63. .

Volume of completed sulphonation mass, 219
gallons. Total time to complete sulphonation, 20
Hours.

NITRATION OF 1:3:6 NAPHTHALENE TRISULPHONIC ACID TO 8:NITRO NAPHTHALENE 1:3:6 TRISULPHONIC ACID.

In order that the nitration be successful, it is essential that it take place at a definite temperature. Patent literature is evidently misleading inasmuch as good results are never obtained by following their directions in laboratory research work.

The nitrator used is similar to a simple type of sulphonator with lower half jacketed and heavily insulated on the outside with magnesia brick. The jacket is used for the circulation of calcium chloride brine solution. The nitrator is provided with mechanical agitation of the horseshoe breaker type, with two and one-half inch outlet at the bottom, with valve and pipe connection to a storage montejus below. The nitrator is installed on a level with the sulphonator, and, as stated before, a two inch pipe connects the two, so that the sulphonation may be blown over by means of air pressure. To dispose of the fumes, a three inch vent is provided, leading to the roof.

Calcium chloride brine solution is cooled by the ammonia process and circulated throughout the intermediate and dye plants from a central storage tank, by means of large rotary circulating pumps. The temperature of the brine is kept as near -20 degrees C. as possible.

After the sulphonation mass has been transferred to the nitrator, brine is circulated through the jacket and the sulphonation is cooled down to a temperature of 10 degrees C. A theoretical amount of a nitrating acid is now added from a storage tank placed above the nitrator, keeping the temperature uniform at 10 degrees to 15 degrees C. The nitrating acid is a mixture of nitric acid and sulphuric acid in the proportion of 37.0% nitric acid, 58.1% sulphuric acid and 5.0% water, 483 lbs of the acid being added to the sulphonation mass. Provided the brine is at the right degree of coldness, it takes about five hours to add the acid. After all the acid has been added, the temperature is held constant at 10 degrees C. for one hour, the brine is blown from the jacket and the mass is heated to 55 degrees C. The mass is held

at 55 degrees C. from one and onehalf to two and one-half hours. If for any reason, plant production is pushed to its maximum, this period may be shortened to one hour. The nitration mass is now dropped to a storage montejus below, preparatory to being blown to the reduction vat.

Inasmuch as the nitration mass crystallizes at a comparatively low temperature, it must be kept warm (at least 50 degrees C.) with steam heated coils either in the montejus or in the nitrator. It is best, however, to arrange the time of nitration so that the mass can be passed to the reducer without delay.

The mass must not be held in the nitrator or the montejus for too long a time, inasmuch as, the nitro group, which is "tacked" onto the nucleus "none too tight" will hydrolize and split off.

A very good check on the hazards which enter into the sulphonation and nitration thus far, is to measure and record the number of inches of nitration mass in the montejus. If this measurement does not remain constant the plant superintendent may look for trouble in any one of the following:-

- (a) Steam condensate from the vent pipe of the sulphonator, dropping back into the sulphonation mass (a very small amount of water will lower the yield over 50%)
- (b) Leaks in the cooling sections of the sulphonator.
- (c) Leak in the jacket of the nitrator, causing an influx of brine or steam condensate, or a loss of nitration out through the jacket.

To test for complete sulphonation or nitration, samples may be taken from each step in the operation and be worked through in the laboratory to the final Amino product, the efficiency determined from this yield.

REDUCTION OF 8:NITRONAPHTHALENE-

1:3:6 TRISULPHONIC ACID TO 8:AMIDONAPHTHALENE

1:3:6 TRISULPHONIC ACID.

The reduction of the nitro (NO_2) body to the Amino (NH_2) body, is carried on in the cold, using iron as the reducing medium. Reduction in most plants is carried out by means of iron in the powdered form (iron filings.) This entails the expense of cast iron reducers, jacketed for brine circulation. In subsequent operations it is difficult to rid the iron, filtration being slow and costly.

In some plants, and according to many patent literature references, the reduction is filtered and milk of lime added to precipitate the excess sulphuric acid as calcium sulphate. The filtrates are then converted to the sodium salt by means of the addition of sodium carbonate (soda ash,) and the calcium carbonate precipitate filtered off. On acidification with hydrochloric acid after the filtrate has been evaporated down, the sodium salt of 8:Naphthylamine (or Amidoaphthalene) 1:3:6 trisulphonic acid is precipitated out.

According to the literature the little extra work necessitated by the production of the calcium salt and the conversion to the sodium salt was counterbalanced by the purity of the Amino body obtained. This we found to be far from correct. Not only did this process require much more apparatus, but the losses resulting from inefficient filtering and washing of the precipitate, and errors committed by the workmen in the care of the filter presses, together with the slow production, offset any advantage the process had over our process.

The high market price of "H" acid and the demand of the intermediate for dyestuffs made quantity production imperative at that time (1918.)

Another method used, offered some advantages. If milk of lime be added after the dilution of the nitration at a specified temperature, the calcium sulphate is precipitated in a granular form and may be efficiently and quickly washed with hot water with a loss of only 0.5% Nitro liquor. The filtrate is then reduced with iron. Soda ash is then added to the reduction liquid whereby, the metallic reduction agent used is precipitated, the

acid used is neutralized, and at the same time the calcium salt is converted to the Amino-sodium salt, by which the calcium is precipitated as calcium carbonate. Even this process, altho more efficient, entails the need of more apparatus, including evaporators.

The method we used seemed to be by far the best and had many advantages including:- small quantity of apparatus; no washing of bulky precipitates; the sodium salt is produced directly; a saving of chemicals; and should, by improper sulphonation, tetra sulphonic salts be obtained, they will remain in solution and pass out along with the excess of sulphuric acid during the filtration, this eliminating all danger of oxy- and dioxy- Naphthalene sulphonic acids being formed in the subsequent fusion process.

The reduction is carried on in a large wooden vat installed on the platform or floor above the sulphonators and nitrators, so that filtration of the small amount of sludge formed may be carried out by gravity, thereby eliminating the need for an extra pressure filtration. The vat is con-

structed of two inch lumber (pine,) is seven feet in diameter, eight feet in height and has a capacity of 2300 gallons. It is lead lined with heavy sheet lead, all seams welded. The vat is provided with a two inch lead coil for brine cooling. The brine enters at the top, passes to the bottom, is coiled around on supported blocks, and passes out at the top. The circulation of the brine coils is protected by a flooring of two inch boards, on account of the fact that empty iron caustic drums is the source of iron for the reduction. For this same reason, two inch boards are hung at intervals around the vat to protect the lead lining from the "caustic cans." The reducer is provided with air agitation, a perforated lead pipe coiled once around the bottom; and an open two-inch steam connection extending about three feet down from the top for heating. The reducer has a wooden cover provided with a hinged door three feet square, and a vent, one foot square, extending to the roof.

The outlet of the reducer is on the side, at the bottom, through a two inch lead line provided with a bronze valve, and leads to a wooden-frame filter press below.

Water is run into the reducer to a height of about thirty-five inches (840 gallons.) If wash water from the press washing of a previous reduction is available, this is run into the reducer from a storage tub, instead of fresh water.

The nitration is now blown from the storage montejus into the water. Air agitation is now turned on, large amounts of nitrous vapors being evolved, escaping through the ventilating duct. The temperature of the mix is now about 50 degrees C. The mix is heated by means of the open steam line to 80 degrees C. Air is blown through the mix for about fifteen minutes or until all evidence of nitrous oxide fumes has disappeared. The mix is now diluted with more fresh water to bring the level in the reducer up to seventy-four inches, a total volume of 1754 gallons. Of this volume, 250 gallons is nitration mass and approximately 1500 gallons is water. This represents a dilution proportion of nitration to water of about one to six, 1500 gallons of water to 250 gallons of nitration mass or approximately 3600 lbs. of water per 100 lbs. of Naphthalene used.

After the final dilution, the cold brine is circulated through the coils and the temperature brought down to 25 degrees C. This normally takes about four hours, but depends upon the temperature of the brine.

650 lbs. of sheet iron (old caustic drums from other plants, previously washed) is now charged into the reducer and the temperature allowed to rise to 35 degrees C. at which temperature it is held constant for twelve hours.

In order to prevent the temperature from rising above 35 degrees C. in the event the brine is not sufficiently cold, it is best to start circulating the brine at about 28 degrees C. The recording chart will then show a smooth curve with a rise in temperature from 25 degrees to 35 degrees C. in about thirty minutes and will hold constant at 35 degrees C.

The most important step in the reduction process is the elimination of all nitrous oxide fumes. If this is not carried out efficiently a diazotization of the Amino group in acid solution will result, with a subsequent "splitting off" of the group, or a

coupling with the naphthol body later in the process with the formation of a dyestuff.

The reduction should be tested for completion about twice a week, by running a sample through to Amino salt in the laboratory. The chemist may test individual reductions for completion by examining the solution for the yellow color of the nitro-group by "spotting" on filter paper. A drop of the reduction on filter paper should be colorless.

FILTRATION OF THE REDUCTION MASS.

This step in the process is necessary where a large amount of sludge is present after the reduction, especially in cases where iron filings have been used as the reducing agent. In case sheet iron is used the amount of sludge is small and the operation may be dispensed with. However, it is a good idea to keep as much mineral matter and dirt as possible from the Amino salt.

The filter press consists of a 22 plate, wooden-frame press, each plate and frame measuring one and one-half inches thick by twenty-four inches square, using heavy wool felt as the filtering medium. The press is provided with a lead-lined drip-pan, and a lead-lined trough which is pitched slightly to allow the filtrate to flow toward one end into a two-inch lead discharge line and thence to the sewer.

In former "H" acid plants, the discharge line led to an air lift, in which, by aerating the solution, there was caused a lowering of the specific gravity, and a rising of the liquor to a second series of wooden tubs used for the precipitation of the Amino salt.

In the more modern plant, a bronze circulating pump of the rotating disk type is used to force the liquor to the precipitation tubs.

The reduction mass is run by gravity through the sludge press and pumped to the precipitation tubs. After the liquor has drained completely, twelve inches of water is added to the reducer and this allowed to gravitate through the press to wash the sludge free from Amino liquor. The wash water is pumped to a wash water storage tank, a small lead-lined wooden tub, installed on a platform above the reducers.

The sludge press is blown dry with air; opened, cleaned, and the sludge washed to the sewer after every fourth reduction.

There are always some pieces of sheet iron left in the reducer. These are taken out after each reduction. If in the course of several reductions, considerable amounts of sludge accumulate at the bottom of the reducer, it is rinsed with water and the sludge washed to the sewer.

THE PRECIPITATION OF 8:AMIDONAPHTHALENE—
1:3:6- TRISULPHONIC ACID TO THE DI-SODIUM
SALT. (AMINO SALT.)

Amido-naphthalene trisulphonic acid, to be in condition for conversion to the naphthol body, must be as free as water and acid as possible. To accomplish this, the Amino liquor is precipitated as a sodium salt, which, when filtered and dried, is successfully converted to the naphthol body by fusion with caustic soda.

The Amino body is soluble in water or dilute sulphuric acid solution, but insoluble in concentrated hydrochloric acid solution. The most efficient method of converting to the sodium salt, and at the same time causing a precipitation, is in the use of sodium chloride.

The precipitation, or as better known in the plant, the "salting" operation, is carried out in large wooden tanks, constructed of two inch planks, approximately eight feet in diameter and eight feet deep, having a capacity of about 3000 gallons. The tanks are wooden-covered for the protection of the workmen. They are provided with mechanical agitators, the agitator being constructed of heavy

wooden cross beams of the breaker type with wooden lugs projecting below the bottom beam to prevent the salt from drifting at the bottom.

About three barrels of salt (280 lbs. per barrel) are dumped into the salting tub to provide a foundation for the liquor.

The reduction is pumped to the salting tank from the reducer after filtration, through the sludge press. The volume of the mass is about 1720 gallons, approximately thirty gallons having been evaporated in the reducer, or lost in the filtration operation. More sodium chloride (common salt) is now added to the reduction liquor making a total of 2500 lbs. The sodium salt of the Amino body is precipitated out as a cream-colored precipitate. Agitation is continued (no temperature control being necessary) for about eight hours, after which time all the Amino salt should be precipitated out.

The volume of the mass after the salt has been added is about 1825 gallons.

A sample of the "salting" is taken to the laboratory at regular intervals, filtered, and the filtrate analyzed for Amino body. This will determine whether sufficient salt has been used or sufficient time given the precipitation.

THE FILTRATION OF THE SODIUM SALT OF THE
AMIDONAPHTHALENE TRISULPHONIC ACID.

The filtration of the "Amino salt" is carried out in large presses of the wooden plate and frame type, constructed of yellow pine and measuring thirty-six inches square and two inches thick. A sufficient number of plates and frames are provided to carry out the filtration of one "batch" or precipitation in one operation. In the event that larger amounts of the Amino salt are to be filtered, the filtration must be carried out in two operations.

The press is provided with a lead-lined drip pan and lead-lined trough with outlet at one end connected to the sewer.

The filtering mediums used is heavy wool felt. This is very expensive and does not last through many filtrations. Heavy #6 duck canvas was tried with success, and although it is much cheaper than the wool felt, deteriorates rapidly in the strongly acid solution. The question remains as to which medium is the cheapest in the end. At the time I left the "H" acid plant, average general operating expenses over a short period of time showed canvas

to have a decided advantage.

Installed near the Amino salt press is a cast iron, lead-lined montejus, used for filtration by pressure. Connecting the salting tank and the montejus is a two inch lead line, interposed at the salting tank and montejus terminals by bronze valves. The line leading from the bottom of the montejus to the press is of iron, lead-lined.

The Amino-salt precipitate is filtered at first by gravity, until the outflow of filtrate from the plate drip-cocks has retarded decidedly. The montejus is now filled and filtration continued by applying air pressure. After all the liquor has been filtered through, low pressure air is applied to the "wash side" of the press for about one hour. This blows almost all excess acid solution from the retained Amino cake and leaves the cake in a position such that it may be easily scraped from the frames into large carts. The carts are provided with rollers so that they may be easily transported from one press to another. For analysis of the Amino filtrate (mother liquor) see section of laboratory analysis, page 88 .



HYDRAULIC PRESSING OF THE WET AMINO-SALT.

For successful conversion to the naphthol body, the Amino-salt must be fairly dry, as stated above. To accomplish this, the wet Amino-salt is separated from its contained acid liquor under twelve inch hydraulic presses with service plates or platforms about five feet square.

Wooden molds or frames, thirtysix inches square by three inches thick, are provided to mold the putty-like Amino-salt into individual cakes for more complete expressing of the acid liquor. The forming of these cakes is accomplished by placing two squares of \$6 duck canvas over each frame, one square with sides parallel to the frame, the other square placed so that its corners are set diagonally to the sides of the frame. The wet Amino-salt is now filled in over the canvas to the top of the frame and the canvas corners turned over. Another cake is made on top of the first, and so on until cakes have been piled to the height of about three feet, the capacity of the press. The rest of the "batch" is molded into cakes and held in reserve until the first pressing is down

sufficiently far so that the capacity of the press will warrant holding the second batch.

The expressing of the liquor in the hydraulic press is accomplished by gradually (within about forty-five minutes) raising the pressure to 2500 lbs. per square inch, and holding the cakes at that pressure until there is no more dripping of liquor. The comparatively dry cakes are, after pressing, from three-quarters to one and a quarter inches thick; and entire batch being pressed down so that it takes up from one and one-half feet to two feet between the platforms of the press. Three hours is usually long enough to press the cakes.

The press is now released, the Amino salt cakes taken out, thrown into carts, weighed, and crushed preparatory to the conversion to the naphthol body.

A small sample is taken from each cake about six inches from the outer edge, sealed in a mason jar, and sent to the laboratory for analysis.

The crushing is accomplished in a spiked rotary-cylinder type of ice crusher, into pieces averaging two inches square.

An average pressed Amino-salt batch will run

about 1050 lbs. for every 350 lbs. of Naphthalene used.

To preserve the canvas, used for the packing Amino-salt, it should be sacked in a sodium carbonate solution after each pressing, otherwise new canvas will have to be supplied for every batch. This step also saves Amino-salt in the long run inasmuch as a weak canvas holding a cake of Amino-salt is liable to split under pressure, scattering Amino-salt in every direction.

For efficiency data on the production of Amino-salt see page 75 .

THE FUSION OF 8:AMIDONAPHTHALENE 1:3:6
TRISULPHONIC ACID (AMINO SALT) TO 1:8
AMIDONAPHTHOL 3:6 DISULPHONIC ACID H.
("H ACID")

If alpha naphthylamine sulphonic acids which have the sulphonic group in alpha-position "8" are submitted to fusion with sodium hydrate the sulphonic group in position "8" is replaced first, and 1: Amino- 8: naphthol(oxynapthalene) sulphonic acid is formed. According to the ease with which other sulphonic groups are replaced, they arrange themselves in the following order:- After the sulphonic group, in position "8" has been replaced, the sulphonic groups in positions 5,6,7,3,2,and 4 are then replaced by the hydroxyl (OH) group. Sulphonic groups in positions 2 and 4 are replaced by the hydroxyl group at high temperatures, or not at all. At high temperatures even the alpha-amino groups can be replaced by the hydroxyl group .

Therefore, even when uniform Amino salt is available. there is the probability of at least two other products, together with "H" acid, forming viz: 1:8 dioxynapthalene 3:6 disulphonic acid (chromotropic acid) and the 1: Amino 6:8 dioxy-

naphthalene 3:Monosulphonic acid. Both of these products interfere with the dyestuff formed from "H" acid; chromotropic acid which produces dyes of red shade, gives to the blue-cast dyes produced from "H" acid, a violet or purplish tinge.

It is therefore very important in the following operation to adhere to directions in regard to the strength of sodium hydrate solutions, the degree of temperature, the pressure and the duration of the operation. A bad fusion can result in the breaking of the Naphthalene ring in extreme cases.

Fusions may be carried out in an open type of fusion pot or in an autoclave. The operation in an autoclave takes longer time for completion but a weaker solution of sodium hydrate may be used, thereby leading to a better control of the fusion.

The caustic fusion is carried out in a 250 gallon gas-heated autoclave provided with horse-shoe type of mechanical agitation, operated at 36 R.P.M. and a three foot cast iron tube to act as an oil well for the extension tube of a #231 Tyco recording thermometer. The autoclave is also provided with a two inch "blow out" line

extending through the top and leading down to the bottom, being bracketed securely in a position near the agitator shaft so that it does not interfere with the operation of the agitator. The autoclave is provided with a pressure gauge, a pressure release line leading from the "blow out" line, and a connection for high pressure air so that the fusion may be blown out after completion to a storage tank installed on a platform above.

After the analysis of the Amino salt has been completed by the control chemist, the charge for the fusion is calculated. An average batch of wet Amino salt will run 60% Amino body and 12% acidity.

For a 250 gallon autoclave, a charge is calculated to have a total volume of about 180 gallons. For this volume a charge of 800 lbs. of wet Amino salt is necessary, this charge being used as the basis of production in this discussion.

The caustic charge is calculated as follows:-

1. Sufficient caustic is necessary to neutralize the total acidity of the Amino salt.
2. For one part of 100% Amino salt, one part

of 100% caustic is used (caustic is calculated from a basis of analysis of 95% - powdered caustic of 95% purity being used.)

3. Sufficient water to dilute the caustic together with the water content of the Amino salt to a 40% solution. (The difference between the weight of wet Amino salt and 100% Amino salt is considered as water and inorganic matter, of which two-thirds is taken as water and one-third inorganic matter.)

Thus a formula for the calculation of the charge may be as follows:-

$$\left(\frac{\text{Wt. of 100\% amino salt} \times 100}{95} \right) - \left(\frac{\text{Wt. of pressed amino salt acidity}}{95} \right) \times 1 = \text{Total caustic.}$$

Of the above:

$$\frac{\text{Wt. of 100\% amino salt} \times 100}{95} = \text{Caustic necessary for 1:1 fusion.}$$

$$\frac{\text{Wt. of pressed amino salt} \times \text{acidity}}{95} = \text{Caustic necessary to neutralize acid.}$$

$$\left(\text{Wt. of pressed amino salt} \right) - \left(\text{Wt. of 100\% amino} \right) \times \frac{2}{3} = \text{water in amino salt.}$$

$$\left(\text{Wt. of 40\% caustic solution} \right) - \left(\text{Total caustic} + \text{water in amino salt.} \right) = \text{amount of water to charged.}$$

The average fusion charge contains the following:-

800 lbs. of Pressed Amino salt.

600 lbs. of 95% caustic.

650 lbs. of water.

The charge of water is put into the autoclave at a temperature of 140 degrees C. or below, which is the temperature to which the autoclave must be cooled from the previous fusions before recharging. powdered caustic soda is now weighed out in its original drum container and shoveled by hand into the autoclave through the charging hole, which is provided with a large funnel like arrangement to prevent the caustic from spilling.

The pressed Amino salt, previously weighed, is now charged into the autoclave and the cover bolted on as quickly as possible. The charging must be done rapidly inasmuch as the residual heat from the previous fusion will cause the mass to foam up, and if the cover is not bolted on in time, will foam out of the autoclave.

As soon as the cover is bolted on, the gas fire is started and the contents heated to about 140 degrees C. (The temperature having cooled down to about 110 degrees C. on adding the charge of water.)

By turning the gas off at 140 degrees C., the autoclave will have acquired sufficient heat to raise the temperature in a smooth chart-curve to 170 degrees C. The heating from 110 degrees C to 140 degrees C takes about one and one-half hours; the heating from 140 to 170 degrees C, about two hours. The temperature is held constant at 170 degrees to 175 degrees C. for one hour and is then raised within half an hour by further gas heating to 180 degrees C., at which temperature it is held for one hour. The temperature is raised again within half an hour to 185 degrees to 188 degrees C. and held constant for half an hour.

With the rise in temperature of the contents, the pressure gauge will show a rise to a maximum of 100 to 110 lbs.

The gas is shut off, air is blown into the fire-box beneath the kettle through the gas burner, and the contents are cooled to about 130 to 140 degrees C. at which temperature the contents may be blown to the storage tank.

The pressure within the autoclave is sufficient to blow the contents to the storage tank. The

blow-out line valve is opened and the contents blown through the two inch line to the storage tank above. When the pressure gauge shows zero pressure, air pressure is admitted to the autoclave and what small amount of the fusion remains is blown to the storage tank.

The autoclave is now allowed to cool preparatory to another charge.

The fusion storage tank is usually placed two floors above the fusion autoclave so that the fusion may be dropped by gravity to the neutralizing tank. It is four feet in diameter, three feet high and has a conical bottom.

In order to aid in the cooling of the fusion from the autoclave to the storage tank, the blow-out line is passed in a coil through a cooling tank and thence into a covered storage tank.

An account is kept of the measurement of each fusion in the storage tank as a check on the fusion operation. Leaks in the autoclave due to the deteriorating and subsequent blowing-out of packing gaskets, cause loss of water in the form of steam, and lead to "overfusion." "Overfusion" may be

detected, also, when the contents are blown to the storage tank by the excessive odor of ammonia, which is an indication of the splitting off of the Amino group and hence a resultant unbalanced final product.

Volume of fusion mass, approximately 170 gallons.

THE NEUTRALIZATION OF THE FUSION MASS WITH THE PRECIPITATION OF THE CONTAINED IRON AS $\text{Fe}(\text{OH})_3$, IN PREPARATION FOR THE FOLLOWING PRECIPITATION AS THE SODIUM SALT OF "H" ACID.

The fusion mass is dropped by gravity to the neutralizing tank, a steel, conical bottom tank, five feet in diameter and four feet high, from the top of the tank to the top of the cone. The tank is lead lined and provided with about four turns of lead coil for cooling with brine. Air agitation is provided by means of an open air line of half inch lead tubing. The bottom of the tank is provided with a two inch lead lined valve leading through a two inch lead pipe to a disk type circulating pump, also lead lined. (note- Lead lined pumps are used in preference to bronze pumps on account of the longer period of service, with less repair.) The circulating line is connected so that it leads to a plate type of sludge press, or by a double valve connection back into the top of the neutralizing tank. The fusion mass in the neutralizing tank is now diluted with water in the proportion of 80 parts of water to 100 parts of fusion mass, or 150 gallons of water to 170 gallons

of fusion mass.

The fusion mass is now cooled to thirty degrees C. by air agitation, by circulating brine through the lead coils. At this temperature twenty degrees muriatic (hydrochloric) acid is added from a lead lined tank above, or by placing carboys of the acid on a wooden support alongside the tank and syphoning the acid into the tank through lengths of rubber tubing. Acid should not be added at a temperature above forty degrees C. or a saponification with the contained sodium hydrate may result in the splitting off of the hydroxyl group.

The mass is treated with the acid until it shows only a faint alkaline reaction or until a sample in a test tube shows a distinct flocculent precipitate of iron hydroxide in the clear liquor. Acidification to the neutral point must be watched very carefully otherwise an excess of acid may result in the precipitation of "H" acid and a subsequent loss of this precipitate in the sludge press.

The neutralized mass is now pumped by means of the centrifugal pump through an iron-plate type of press (Albright & Nell) with #6 duck canvas as the filtering medium and the clear filtrate returned

from the press trough to a second lead lined conical bottom tank similar to the one used for neutralization.

Live steam is now turned into the "wash side" of the press for about fifteen minutes in order to dissolve out "H" acid precipitate that may have resulted in the neutralizing process, and the press contents washed with about 150 gallons of hot water, which is turned back into the neutralizing tank and used as the diluent for the next fusion. A measure of the amount of wash water to be used may be obtained by calibrating the neutralizer and filling with wash water to a specific point.

Average amount of acid used for the		
neutralization	- 1150 lbs. -	118 Gals
Average volume of fusion mass	-	170 "
Average volume of water diluent		<u>165 "</u>
		453 "

The sludge press is blown dry with air, cleaned after every filtration, and the sludge washed to the sewer. The sludge may be tested for "H" acid content by adding hydrochloric acid to a small portion and examining for the cream-colored precipitate of "H" acid. If "H" acid is found, the sludge may be

returned to the neutralizer and the iron re-precipitated with the next fusion.

Note:-

If an excess of acid is accidentally added to the fusion, thereby, precipitating a portion of the "H" acid, the mass may be brought back to alkaline solution by adding a solution of sodium hydrate. This procedure will save much work in the filtration of the sludge and will prevent a loss of "H" acid. It is not well, however, to rely upon this method, inasmuch as, it results in an unaccountable loss of "H" acid.

THE PRECIPITATION OF THE SODIUM SALT OF "H" ACID.

The precipitation tank is similar in all respects to the neutralizing tank, except that it is provided with a wooden cover and a wooden duct leading to the roof, which duct is provided with a steam injector to induce a draught to take off the sulphur dioxide fumes formed from the sodium sulphite in the fusion mass upon acidification.

Hydrochloric acid, 20 degrees Baume', is now added to the partially neutralized fusion mass until it is thoroughly acidified as shown by a permanent acid test on Congo red paper, after fifteen minutes of air agitation.

Upon acidification the mass undergoes a change in state and color from a clear brown colored liquor (neutral) through a grass green stage (partial acidification) to a thick cream-colored mass of precipitated sodium salt of "H" acid.

The precipitate is now dropped to a flat bottomed wooden tank provided with a wooden cover, wooden hinged opening and a wooden ventilating duct which leads into the acidifier duct above. The

precipitate is allowed to remain in the wooden tank for about three hours to thoroughly crystallize out all the sodium salt of the "H" acid.

Total volume in neutralization tank	453 gals.
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Hydrochloric acid needed to complete acidification -690 lbs.	<u>72 gals.</u>
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Total volume in acidifier	525 gals.
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FILTRATION OF THE SODIUM SALT OF 1:8 AMIDO
NAPHTHOL 3:6 DISULPHONIC ACID H (H-ACID.)

The procedure for the filtration of "H" acid is analogous to that of Amino salt filtration, except that more care is excercised in the "dumping" or cleaning of the filter press from the workman standpoint on account of the sulphur dioxide fume.

From the wooden "intermediate" or crystallizing tank the precipitate is allowed to flow by gravity to the wooden plate and frame press, of the same type and size as the Amino salt filter press, until the filtrate runs in a very slow stream. The balance of the precipitate is dropped to a lead lined montejus and forced from there through the press by air pressure. All lines through which the "H" acid precipitate passes are of two inch lead pipe.

A sufficient number of plates and frames are added to the press to filter the entire batch of "H" acid in one operation. For a plant operating at normal efficiency, using an 800 lb. charge of pressed Amino salt per fusion the anticipated volume of pressed precipitate may be taken as twenty cubic feet. For this volume a press of twenty-four frames,

thirty-six inches square and two inches thick, is more than ample. Heavy wool felt is used as the filtering medium.

On account of the action of the sulphurous acid on the wooden filter plate, care must be used when filtering under air pressure. As a rule, twenty lbs. per square inch of pressure on the montejus is sufficient, but the press must be closely watched for the weakening and breaking of the plates and loss of "H" acid with the filtrate. The filtrate running from the plate drip-cocks, must be a clear brown color, a creamy or milky filtrate denotes a torn medium or broken plate. In this event, the troublesome plate is "blocked off" by closing its drip-cock. During the filtration a sample of the filtrate is obtained and taken to the laboratory for analysis. The result is reported as the percentage loss of "H" acid in the mother liquor. This loss averages about 1.00%, so that with a total volume of about 4800 lbs of filtrate the "H" acid loss will not total more than 48 to 50 lbs.

After all the precipitate has been blown into the press, air is blown through the "wash side" of the press for about forty-five minutes in order to

dry the precipitate as much as possible. Air is blown through the precipitate until filtrate ceases to drip from the cocks. The dryer the precipitate, the easier the clearing of the press and the smaller the loss of "H" acid in the hydraulic pressing operation.

The filtration takes about three hours.

The press is now opened, the "H" acid precipitate scraped from the plates and frames with wooden blades into low, four-wheeled carts, and taken to the hydraulic presses.

For a long time the problem of hiring and retaining labor to clean the "H" acid presses was a difficult one to solve. It was almost impossible for a man to clean precipitate for more than a five minute period, on account of the fumes of sulphurous acid gas, even with the use of so-called efficient respirators. Long periods of work under these conditions, result in weakening of the lungs with the attendant bleeding from the nose and mouth,

In order to relieve this condition under which the men were compelled to work, it seemed that the only practical solution was the installation of an efficient ventilating system. A long rectangular

duct, the width and length of the "H" acid press was built directly over the press with about eighteen inches clearance. In order to aid in the induction of draught, the ventilating duct or "box" was divided into two foot sections, and from the division line of each section a sheet of oil-skin long enough to reach to the top of the press, was attached. The rectangular duct was connected directly to a large four-footed blower. Sufficient draught was induced to eliminate the fumes to a point where the workmen could work with a minimum of danger, provided a muzzle type of respirator be used as an added precaution.

HYDRAULIC PRESSING OF THE WET "H"-ACID.

In order that the "H" acid may be in suitable condition, either for transferring to the dye plants for direct coupling and conversion into dye, or for drying in the vacuum dryer and milling for shipment, it must be separated from moisture as much as possible by subjecting it to pressure under the hydraulic press.

The description of the operation of forming into cakes and pressing is identical with the pressing of Amino salt and will not be repeated here. After pressing for about three hours, the cakes are taken from the press, crushed into pieces about one inch square in a rotating drum type of ice crusher, similar to the one used for amino salt crushing, and packed into barrels. A representative sample is obtained, packed in a mason jar, labeled with the batch number, and taken to the laboratory for analysis.

An average batch of "H" acid will weigh about 500 lbs. and will average about 60% "H" acid. For the analysis of "H" acid see section on methods of analysis, page For yield and efficiency of "H" acid see section on plant efficiency, page 75 .

DRYING AND MILLING OF "H" ACID PREPARATORY
TO STORING OR SHIPPING.

"H" acid from the hydraulic press and crusher is packed onto trays and the trays shelved in the vacuum dryer. (any type dryer will suffice, Gordon, Buffalo Foundry, etc.) The product is dried at 80 degrees C. under a vacuum of twenty-six inches for twenty-four hours. The dried cake may be packed directly into barrels for storage or may be milled.

Milling is carried out in a mushroom type of ball mill, using iron balls about three inches in diameter. An average ball mill charge is 100 to 150 lbs. of "H" acid. The product is milled to a fine, smooth powder and packed in barrels for shipment. The average analysis of dried and milled "H" acid runs about 80.0%

For plant yield and efficiency see page 75 .

APPROXIMATE TIME ALLOWANCES OF THE
VARIOUS OPERATIONS.

Sulphonation - 18 to 20 hours.

Heat 160 degrees C.	45 min.
Adding 18 oleum	1 hours
Heat to 170 degrees C.	15 min.
Hold at 170 " C.	1 hour.
Cool to 95 " C.	$3\frac{1}{2}$ "
Add 25 oleum	$1\frac{3}{4}$ "
Hold at 95 degrees C.	2 "
Heat to 180 " C	$1\frac{1}{2}$ "
Hold at 180 " C.	6 "
Cool before blowing	1 "

Nitration - 8 to 9 hours.

Brine cooling to 10 degrees C	5 hours
Adding mixed acid	1 "
Heat to 55 degrees -60°C	$\frac{1}{2}$ "
Hold at 55 " C	2 "

Reduction - 15 hours.

Heat to 80 degrees C.	15 min.
Agitation	30 "
Cool to 25 degrees C.	3 hours.
Hold at 35 " "	12 "

Salting. - 8 hours.

Amino Salt Filter Press.

Time to filter	3 to 5 hours.	
Air drying	1	"
Dump & clean press	1	"

Hydraulic Pressing.

Packing in cakes	2	"
Pressure to 2500 lbs.	2	"
Pressure at "	2	"

Fusion.

Charging of caustic, water

and amino salt	1	"
Heat to 140 degrees	1 $\frac{1}{2}$	"
Heat to 170 "	2	"
Hold at " "	1	"
Heat to 180 "	$\frac{1}{2}$	"
Hold at " "	1	"
Heat to 190 "	$\frac{1}{2}$	"
Hold at " "	$\frac{1}{2}$	"
Blow up fusion	$\frac{1}{2}$	"

Neutralization.

Cooling to 30 degrees C	1 $\frac{1}{2}$	"
Adding 20 acid	1 $\frac{1}{2}$	"
Filter through sludge press	1	"

Acidification.

Acidifying	$\frac{1}{2}$ hour
------------	--------------------

Holding in crystallizer	3 "
-------------------------	-----

"H" acid filter press.

Filtration	$1\frac{1}{2}$ "
------------	------------------

Air drying	1 "
------------	-----

Hydraulic pressing.

Packing	1 "
---------	-----

Pressure to 2500 lbs.	2 "
-----------------------	-----

Pressure at " "	2 "
-----------------	-----

Average elapsed time between starting a
sulphonation and producing Amino salt—65 hr.

Average elapsed time between starting fusion
and producing "H" acid—24 hrs.

Average elapsed time, sulphonation to final
product—90 hrs.

SCHEDULE OF PLANT OPERATION.

In a plant producing about 30,000 lbs. of "H" acid per month, there is required two sets of apparatus, that is, two sulphonators, one nitrator, two reducers, etc. In order to arrange a schedule so that but one nitrator and one amino salt filter press will be necessary, the sulphonations must be timed about 12 hours apart. This arrangement of schedule is necessary at the amino salt end only, the fusion end not requiring a schedule inasmuch as the steps in the process at this end are not of a conflicting nature.

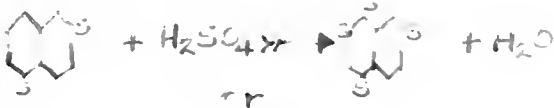
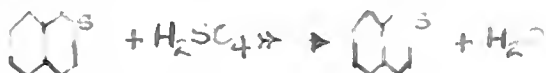
Schedule	Set No.1	Set No.2
Sulphonation start	7:30 AM	7:30 PM
" finish	1:00AM(2d day)	12:30 PM (2d day)
Nitration start	7:30AM "	3:30 PM "
" finish	3:00PM "	2:30 AM "
Reduction start before	7:30PM "	7:30 AM "
" finish	" 7:30AM(3d day)	7:30 PM (3d day)
" filtered by	10:30AM "	10:30 PM "
Salting start	10:30AM "	10:30 PM "
" finish	6:30PM "	6:30 AM "
Filtration started	6:30PM "	6:30 AM "
" completed	11:30PM "	11:30 AM "



Press cleaned by	12:30 AM	12:30 PM (3d day)
Amino salt packed by	2:30 AM	2:30 PM "
Hydraulic pressing		
completed by	7:30 AM(4th day)	7:30 PM (4th day)

Thus, it may be seen from the above schedule that with two sulphonators and but one nitrator and one filter press and hydraulic press that by starting the batches 12 hours apart, they will not conflict. Of course, in order to accomplish this, it is necessary to have two sets each of reducing tanks and salting tanks, altho but one reduction press is necessary for the reduction filtration.

REACTION FORMULAE OF THE "H" ACID PROCESS.



"S" = SO_3H .

Mol. Wt. (128.11 + 3(98) \rightarrow 368 + 54.)

To compute amount of Sulphonic acid taken up by the sulphonic groups.

Naphthalene (128) : Sulphonic acid(294) : : lbs.

Naphthalene (100) : X.

X = 430 lbs. of 100% Sulphuric Acid.

Therefore \div 350 lbs. Naphthalene requires
1505 lbs. 100% H_2SO_4 .

490 lbs. of 18% H_2SO_4 (104.05% H_2SO_4) = 510 lbs.
of 100% H_2SO_4 .

2450 lbs. of 25% H_2SO_4 (105.63% H_2SO_4) = 2584 lbs.
of 100% H_2SO_4 .

3094 lbs. 100% H_2SO_4 .

3090 - 1505 = 1589 lbs. of 100% H_2SO_4 left as excess
acid after the sulphonation.

Nitration.

Nitric acid required for nitration (theoretical
amount is used)



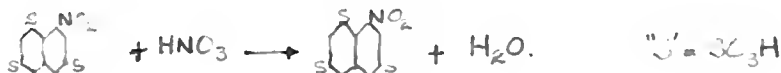
Mol. Wt. Naphthalene (128) : Mol. Wt. Sulphonic acid (368) : : 350 : X.

X = 1010 lbs. Sulphonation mass. (Exclusive of excess acid.)

Mol. Wt. Sulphonation mass. (368) : Mol. Wt. Nitric acid (63) : : 1010 : X.

X = 175 lbs. of 100% Nitric acid.

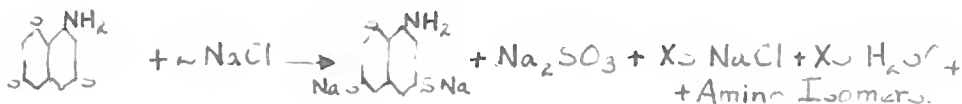
= 483 lbs. of 36.5% Nitric acid.



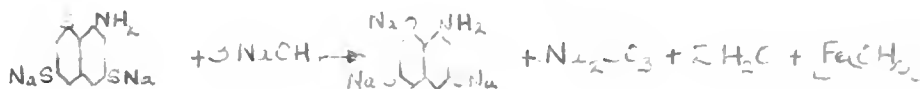
Reduction.



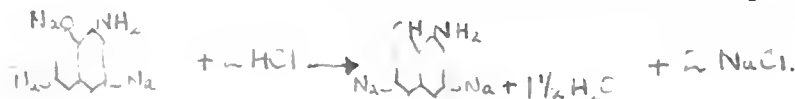
Precipitation.



Fusion.



Neutralization & Precipitation.



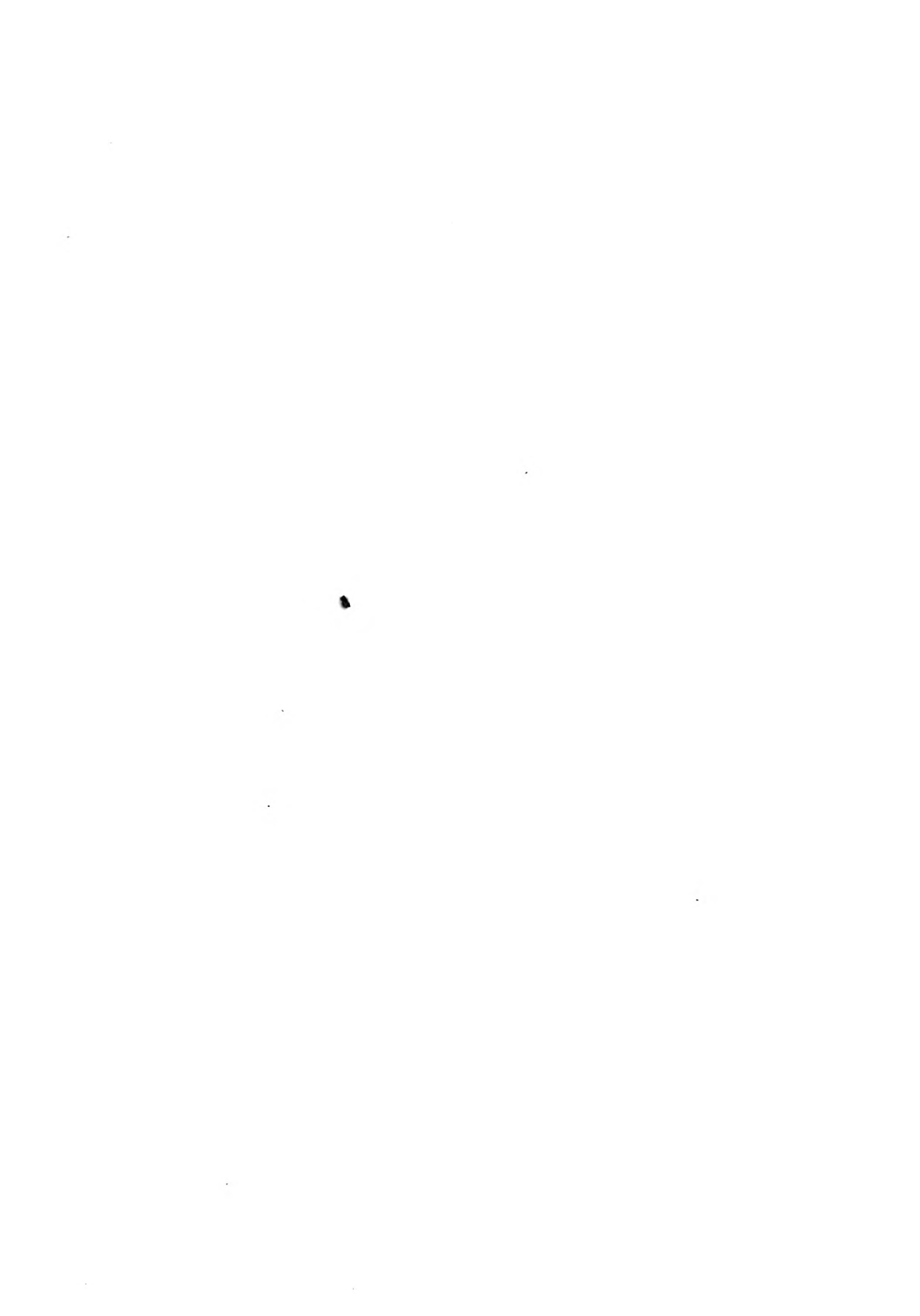
RAW MATERIALS USED IN THE "H" ACID PROCESS.

"H" acid plants are, as a rule, but one unit of a large dye plant and intermediate organization. For this reason, the problem of raw material delivery becomes a comparatively simple one, inasmuch as a large acid storage space is available and necessary to supply all the other dye and intermediate units.

Sulphuric acid of all strengths (percentages of excess SO_3) is usually stored in large iron tanks, dropped to large storage montejus and blown by air pressure over covered iron lines to the storage tanks of the various plants.

Mixed acid having a corrosive action on iron is stored in glass carboys of 172 lb. capacity, and delivered to the various plants in this container.

Iron for the reduction process is delivered to the plant on flat cars. If the general plant uses large quantities of commercial caustic soda, the problem of the utilization of the iron drums is solved, otherwise sheet iron or waste caustic drums must be bought from other sources.



Naphthalene is shipped to the plant in sacks, each containing about 300 lbs.

Salt (sodium chloride) is shipped either in bags or barrels.

Caustic soda is shipped in sheet iron drums containing 650 to 750 lbs. and may be in solid or powdered form, depending upon the method of dilution used.

Hydrochloric acid is delivered in carboys of 113 lbs. net acid content.

SPECIFICATIONS FOR RAW MATERIALS.

Naphthalenemelting point 79.3 C.

18% Oleum (sp.gr. 1.883) . .104.05% H_2SO_4

25% Oleum (sp.gr. 1.9125) . 105.62% H_2SO_4

Mixed acid { 37.9% HNO_3
 { 57.5% H_2SO_4
 { 4.6% H_2O

Sodium hydrate (powdered) . { 76% Na_2O
 { 94% $NaOH$
 { Not over 3% Na_2CO_3
 { Not over 2% $NaCl$

18% Be' Hydrochloric acid .. 27.92% HCl

sp.gr. 1.142

MASS VOLUMES IN VARIOUS OPERATIONS IN THE
MANUFACTURE OF "H" ACID, CORRESPONDING TO
350 LBS. OF NAPHTHALENE.

In sulphonator (400 gals. total capacity)

Naphthalene	350 lbs.	32.5 gals.
18% Oleum490 "	32.0 "
25% "	<u>2450 "</u>	<u>.154.5 "</u>
Total mass	3290 "	219.0 "

In nitrator (500 gals. total capacity)

Sulphonation mass ,	3290 lbs.219.0 gals.
Mixed acid	<u>483 "</u>	<u>.40.0 "</u>
Total mass	3773 "	259.0 "
Sp.Gr. nitration mass.	1.83	

In reducer (2300 gals. total capacity)

Nitration mass . . .	3773 lbs.259.0 gals.
Water of dilution . ---	1510.0 "
Iron	650 "	<u> </u>
Total volume	1769.0 "
Sp. Gr. of reduction mass . . .	1.18	

In salting tub (3000 gals. total capacity)

Reduction mass before salting . . .	1720.0 gals.
Salt	2520 lbs.
Total volume after salting	1834.0 "

In filter press (30 frames)

Total volume of 30 frames(2"36"36") . . 40.cu.ft.

Total volume of precipitate (average)225 gals.

30 cu.ft.

Volume of filtrate 1725 gals.

Autoclave (250 gals. total capacity.)

Amino salt800 lbs.

Caustic600 "

Water650 "

Total volume of fusion mass 2050 lbs. 170.0 gals.

In neutralizer (700 gals. total capacity)

Volume of fusion mass170.0 "

Water of dilution1375 lbs. 165.0 "

Volume after dilution 335.0 "

Hydrochloric acid added (average)1150lbs.118.0 "

Total volume 453.0 "

In acidifier (700 gals total capacity)

Total volume in acidifier 453.0 "

Additional acid 690 lbs. . . 72.0 "

Total volume of precipitated mass 525.0 "

Filter press (24 frames)

Volume of precipitate 20.cu.ft.

Total volume of 24 frames (2" 36" 36")	35. cu.ft.
Volume of filtrate	4800 lbs.
Sp.gr. of filtrate	1.12

PLANT ORGANIZATION.

For a plant producing 60,000 lbs. of "H" acid per month, a working schedule of 24 hours per day must be in force. The 24 hour schedule is divided into three shifts of eight hours each viz: 7:30 AM to 3:30 PM, 3:30 PM to 11:30 PM and 11:30 PM to 7:30 AM the following day.

The chief executive of the plant is the Department Superintendent. Under the Superintendent and in direct charge of all plant operations and laboratory control is the Chief or Works Chemist.

The plant personnel is made up as follows:-

	For each shift	total
Shift foremen	1	3
Chief operators	1	3
Sulphonation operators	1	3
" " ass't.	1	3
Reduction & salting oper.	1	3
" " ass't.	1	3
Fusion operators	1	3
" " ass't	1	3
Acidification operator	1	3
Press operators	1	3
Press cleaners	2	6
Plant laborers	4	12

Amino salt & "H" acid	(day work)	2
Grinding	"	1
Janitor	"	1
Office clerk	"	1
Control chemist	"	1
Research "	"	1

PLANT EFFICIENCY.

Process or plant efficiency is computed on a production basis in pounds of product per pound of basic product, used (in our case, naphthalene) instead of on a percentage basis; which is usually computed as the proportion of final product to the theoretical yield.

For instance, computing from the molecular formulae the theoretical production is as follows:-

1 lb. naphthalene (mol.wt.128.1) = 3.33 lbs.

amino salt (mol.wt.427.)

1 lbs. naphthalene (mol.wt.128.1) = 2.875 lbs.

"H" acid (mol.wt.368.)

1 lb. amino salt (mol.wt.427) = .861 lbs. "H" acid

(mol.wt.368.)

Average process production figures show the following equivalents:-

1 lb. naphthalene = 1.70 lbs. amino salt.

1 lb. amino salt = .63 " "H" acid.

Therefore:-

1 lb. naphthalene = 1.071 lbs. "H" acid. (This last figure is taken as the plant overall efficiency.)

From the above average process yields and the theoretical yields we can compute plant efficiency

on a percentage basis simply for comparison.

Yield of amino salt from naphthalene

$$\frac{1.70}{3.53} = 51.2\%$$

Yield of "H" acid from Amino salt

$$\frac{.63}{.861} = 73.1\%$$

Yield of "H" acid from naphthalene

$$\frac{1.071}{2.875} = 37.4\% \text{ (overall efficiency)}$$

By studying the above figures, it can be readily seen that the actual yield in comparison to the theoretical yield is very low. It is doubtful whether the plant efficiency can be raised very much above this on account of the character of amidosulphonic acids and amidonaphthol sulphonic acids.

To compute the above efficiency, all figures are based on 100% product.

For Amino Salt

$$\frac{\text{Lbs. pressed amino salt} \times \text{analysis in \%}}{\text{Lbs. naphthalene used} \times (350)} = \text{efficiency}$$

For "H" acid

$$\frac{\text{Lbs. pressed "H" acid} \times \text{analysis in \%}}{\text{Lbs. pressed amino salt used} \times \text{analysis in \%}} = \text{efficiency}$$

Plant overall efficiency.

$$\text{Amino salt efficiency} \div \text{"H" acid efficiency} = \text{overall efficiency.}$$

In connection with the plant efficiency and cost data, the following approximate figures are interesting:-

For One Month's Operation.

Number of sulphonations made	134
Naphthalene consumed(lbs.)	50,250
Production of amino salt (lbs.)-100%	83,456
Average production per sulphonation(lbs.)	623
Amino salt produced per lb. of naphthalene consumed (lbs.)	1.66
Amino salt consumed in "H" acid production lbs.	83,345
Number of fusions made	179
Production of "H" acid (lbs)100%	52,837
Average production per fusion (lbs)	280
"H" acid produced per lb. of amino salt consumed (lbs.)	.633
"H" acid produced per lb. of naphthalene consumed (lbs.)	1.052

From the above figures the plant efficiency is derived.

Amino Salt Efficiency.

(Amino salt produced per lb. of naphthalene consumed.)	1.66
---	------

"H" acid efficiency.

("H" acid produced per lb. of amino salt consumed.)	.633
--	------

Overall efficiency.

("H" acid produced per lb. of naphthalene consumed.)	1.052
---	-------

"H"ACID EFFICIENCY: INVESTIGATION OF
"H" ACID LOSSES.

The cause of the low efficiency of "H" acid production is not definitely known, except for the known peculiarities of the sulphonic acids. An investigation into the "H" acid loss in each step of the process will reveal the step wherein the greatest loss will be found and the step which should receive the greatest amount of attention. By analyzing every step in the process and calculating the amount of 100% "H" acid therein, it is possible to locate just where the greatest loss occurs.

Fusion #435(23" in storage tank)(using a laboratory sample of 1000 grams.)

Sample (SP.GR.1.5)(Representing)	2242.5 lbs. (Approx.)
NaNO ₂ analysis	28.15%
Diazo "	<u>27.90%</u>
Average %	28.02%
100% "H" acid	627.7#

AFTER DILUTION WITH WATER.

Wt. of fusion mass.	2242.50 lbs.
Water added	<u>1400.0</u> "
Total wt. of diluted mass	3642.50 "

NaNO ₂ analysis	17.00%
Diazo "	<u>17.05%</u>
Average %	17.02%
100% "H" acid	627.20 lbs.
100% "H" acid before dil.	<u>627.20 "</u>
Loss of "H" acid	000.000 "
% loss in dilution step	000.000 "
AFTER 1ST ACIDIFICATION WITH HYDROCHLORIC ACID.	
Wt. of diluted mass	3643.50#
HCL added	<u>1265.00#</u>
Total Wt. (SP.GR.1.2)	4907.50#
NaNO ₂ analysis	12.35%
Diazo "	<u>11.30%</u>
Average %	11.82%
100% "H" acid	579.10#
100% "H" acid after dil.	<u>627.20#</u>
Loss of "H" acid	48.10#
% loss in 1st. acidification	6;10%
100% "H" acid in original sample	627.20#
100% "H" acid after 1st. acid	<u>579.10#</u>
Loss of "H" acid	48.10#
% loss	7.7%

AFTER 2ND ACIDIFICATION & HYDRAULIC PRESSING.

Press cake	488.00#
NaNO ₂ analysis	59.79%
Diazo "	<u>59.00%</u>
Average % analysis	59.38%
100% "H" acid	289.30#
100% "H" acid production	289.80#
100% "H" acid after 1st. acid	<u>579.10#</u>
Loss	289.80#
% loss	50.04%
100% "H" acid in original sample	627.70#
100% "H" acid in press cake	<u>289.30#</u>
Loss	338.40#
% loss	53.90%

MOTHER LIQUOR

Wt. estimated	4879.50#
NaNO ₂ analysis	1.27%
Diazo "	1.02%
Average %	1.10%
100% "H" acid in sol.	48.79#
100% "H" acid in press cake	<u>289.30#</u>

SLUDGE

Wt.	67.50#
NaNO ₂ analysis	4.02%
Diazo "	.50%

Average %	2.26%
100% "H" acid	1.48#
TOTAL AMOUNT OF 100% "H" ACID ACCOUNTED FOR	
After 1st. acid	4907.50#
2nd. HCL added	<u>460.00#</u>
Total	5367.50#
Press cake	488.00#
Est. Mo. liquor	4879.50#
Average %	1.00%
100% "H" acid in mo. liquor	48.79#
100% "H" acid in press cake	289.30#
100% "H" acid in sludge	1.48#
100% "H" acid in wash water	<u>2.66#</u>
Total 100% "H" acid acct'd for	343.23#
Total 100% "H" acid calc'd.	<u>627.70#</u>
Loss over that calc'd.	285.47#
% loss	45.40%

COMPARISON OF LOSSES IN PERCENT

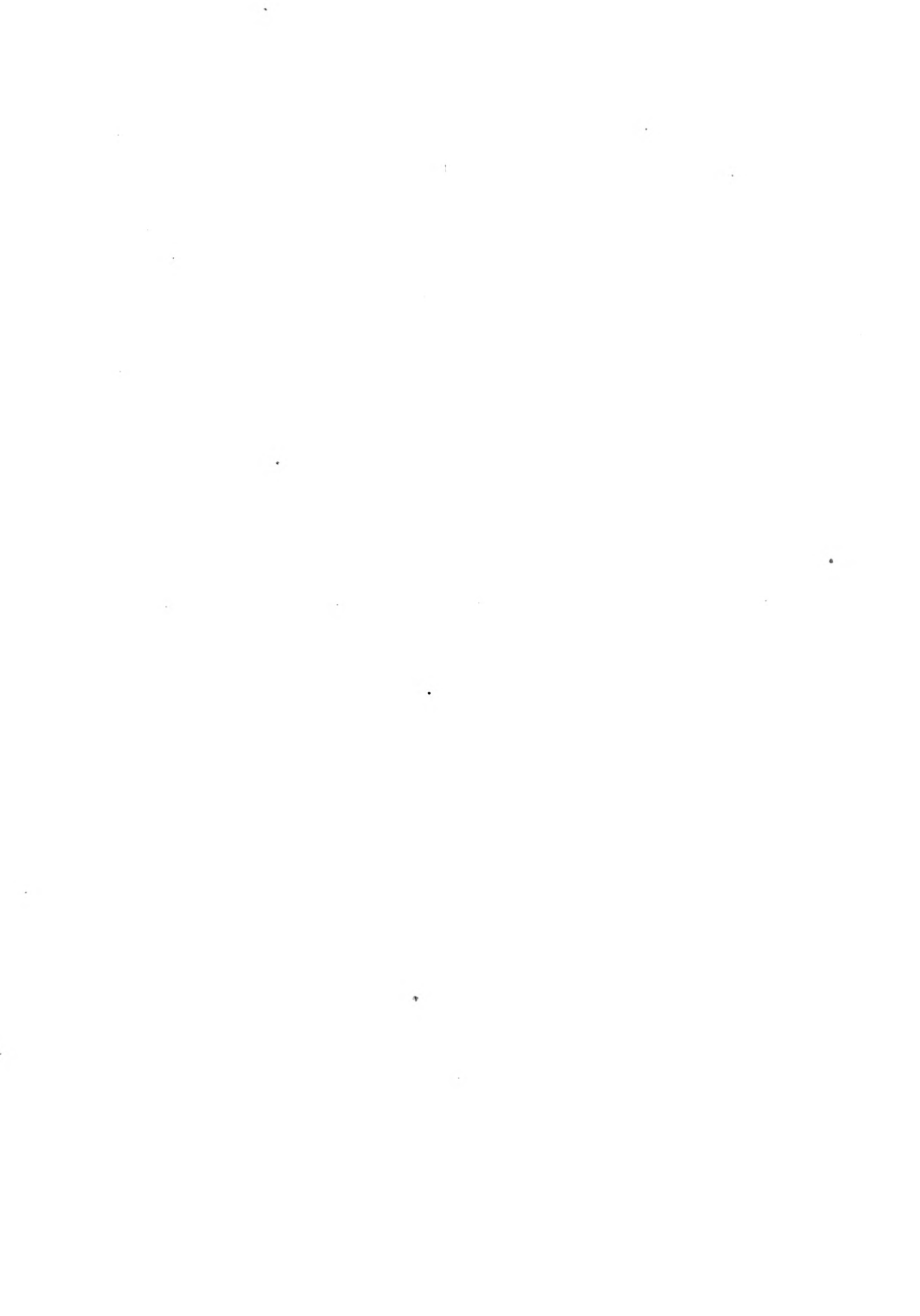
In plant	In laboratory
From original sample to dil. 1.70%	Gain 0.32%
" dil. to 1st. acid 6.10%	8.20%
" original sample to 1st. (acid) 7.70%	7.90 %
" 1st. acid to press cake 50.04%	54.10%
" dil. to press cake 53.10%	53.4 6 %

From orig. sample press cake	53.90%	53.30%
Acc. for over that calc'd	45.40%	44.70%

Efficiency in the plant was 58.80%

It appears from the above results that the loss in yield of "H" acid occurs in the second acidification or precipitation of the "H" acid. One would think that this loss would be manifested in the mother liquor and wash water, Upon carefully titrating the mother liquor and wash water, however, it was found to contain an average of 1.00%, and the wash water but 0.1% "H" acid.

The acidification process, therefore, will bear a great amount of research work. It is my opinion that in the acidification and precipitation there is a rapid saponification or splitting of the amidonaphthol disulphonic acid forming a soluble sulphonic body, without amino and the hydroxyl groups.



COST OF PRODUCTION OF "H" ACID

(Approximate figures, for comparison only.)

In considering the cost of production of any manufactured product, the item of raw material although very important, is but one of many. Other important items entering into consideration are: operation labor, repairs and maintenance, handling of supplies, shipping expense, special repairs, distribution expense and works general expense.

PLANT DISTRIBUTION EXPENSE may be itemized as follows:- Amino filter presses, including new frames and woolen or canvas medium; "H" acid presses; hydraulic presses; electrical equipment; piping, including that used in plant product transmission only; and miscellaneous equipment and sundries, including wooden shoes for laborers, brooms, cleaning compounds, rubber hose, office supplies, gas fittings, sawdust, pails, shovels, rubber gloves, and laboratory supplies.

WORKS GENERAL EXPENSE may be itemized as follows: machine shop and pattern shop expense, control and research laboratory expense, handling of raw materials, handling of acids, brine expense, electric light

and power, compressed air, water, steam, personal injury and reclaiming expense, building, safety devices, recording and measuring instruments, piping, tools and miscellaneous supplies, lubricants, new machinery, material loading and packing, purchases power and gas. (The item of interest on investment, etc. does not enter into this discussion.)

For a plant of 50,000 to 60,000 lbs. production per month, expenses would itemize as follows:

Item	Total expen.	expen. per lb. "H"A. pro. (52,807lb.)
Raw material for amino salt	\$15639.00	\$0.296
Raw material for "H" acid	10371.00	.196
Operation labor	9428.00	.179
Repairs and maintenance	(Labor 3339.00 Maint 6338.00	(.063) (.120)
Handling supplies	1094.00	.021
Shipping expense	342.00	.006
Works general	7942.00	.15
Special repairs	595.00	,001
Distribution expense	<u>2793.00</u>	<u>.063</u>
Total expenditure	57,881.00	1.095

Expenditures for distribution expense items are as follows:

Amino filter presses	1360.00	.026
"H" acid filter presses	1277.00	.024

Hydraulic presses	\$1590.00	\$.031
Electrical equipment	793.00	.015
Piping	2359.00	.044
Miscellaneous	<u>2294.00</u>	<u>.043</u>
Total expenditure	9673.00	.183

The above expenditures are incident to the cost of labor, raw materials and supplies in 1918. At this time "H" acid was listed in the market reports at \$3.00 per lb. The present market price of "H" acid is \$.90 to \$1.00 per lb. A comparison of the current market prices of raw materials is as follows:

Material	1918	1922
Naphthalene	\$.06	\$.070
18% oleum	.01	.008
25% oleum	.02	.014
Caustic soda	.0275	.030
Hydrochloric acid	<u>.015</u>	<u>.01</u>
	.1325	.132

From this data it would appear that the cost of materials in 1922 has lessened, but a very small amount under the cost in 1918.

Therefore in order to operate at a profit we must look to the cost of labor and the plant efficiency for a reduction in production cost.

LABORATORY ANALYTICAL METHODS.

Amino Salt.

Sample:- 10 grams of the wet pressed amino salt. Dissolve in 500 cc of water in a volumetric flask. Pipette off 50 cc aliquot part (equivalent to 1 gram of sample.) Add 5 cc of hydrochloric acid CP, 50 cc. distilled water in a 400 cc. beaker. Cool beaker and contents in a bath of ice and water. Titrate with N/10 sodium nitrate to an immediate blue color when tested on a spot plate with potassium iodide - starch solution after standing about one minute.

Standardization Of N/10 Sodium Nitrate Solution.

Dissolve 7.35 grams of sodium nitrate CP in one liter of distilled water. Standardize in the cold against 0.5 gram pure tolidin, recrystallized from alcohol. melting point 129 degrees C., crystallizing point 126.5 degrees C.; molecular weight, 212.2.

$$1\% \text{ N/10 NaNO}_2 \equiv .0106 \text{ grs. tolidin } \left(\frac{212.2}{2} \right)$$

$$0.5 \text{ gr. tolidin} = 53.5 \text{ cc nitrate solution}$$

$$\frac{0.5}{53.5} = .00938 \text{ gr. tolidine lcc nitrate}$$

$$\frac{.00938}{.0106} = .88 \text{ Normal N/10}$$

$$\text{Amino salt factor} = 427 .88$$

Potassium Iodide - Starch Solution.

2 grams starch in 400 cc. water, boil, add 1 gram potassium iodide, 2 grams zinc chloride or chloroform.

Acidity Of Amino Salt.

Pipette 50 cc. amino salt solution. Titrate with N/5 sodium hydrate solution.

Analysis Of Amino Salt Mother Liquor.

25 cc. of mother liquor, dilute to 250 cc. add soda ash till alkaline. Pipette 100 cc aliquot part with N/10 sodium nitrate.

$$1\text{cc. N/5 NaOH} \equiv \frac{.049}{5} \equiv .00999 \text{ grams H}_2\text{SO}_4$$

ANALYSIS OF "H" ACID.

In the analysis of "H" acid, both sides of the product must be accounted for, the naphthol or diazo side, and the amino side. In the analysis, both sides must be balanced, that is for an amino percentage of 60.0 there must be a diazo percentage near 60.0. An increase in percentage of the diazo group over the amino group denotes an over-fusion. Therefore, this analysis of "H" acid results in the control of plant fusions and a control of uniformity of product.

Amino Group.

Weigh 10 grams of the pressed "H" acid into a 400 cc. beaker, add 300 cc. of distilled water, 2 grams sodium bicarbonate and allow to stand a short time to dissolve the "H" acid. Transfer to a volumetric flask and make up to 500 cc. Pipette 50 cc into a 400 cc beaker, make slightly acid with hydrochloric acid (about 6cc,) and cool in an ice water bath to about 4. degrees C. Titrate with N/10 sodium nitrate as in amino salt analysis. For an exact determination of "H" acid proceed as follows:-

The Accurate Determination of "H" acid With Sodium Nitrate.

To 2,000 grams of "H" acid in a 600 cc. beaker, add 200 cc. of distilled water, and 20 cc. of concentrated hydrochloric acid. Since "H" acid is veryhydroscopic the weighing is done rapidly. It is not essential that the "H" acid be dissolved; which of course is impossible in such small volume. Set the beaker in melting ice and ice water until cold, (invariably 4 degrees C.) and titrate cold with a tenth normal solution of sodium nitrite. "H" acid titrating 92.05% would require exactly 50 cc. of a solution exactly tenth normal; in practice it is found more convenient to have the nitrite from 1.07 to 1.09 times tenth normal for the titration of 2 grams "H" acid (also 0.5 gr. Tolidin, Alpha- Naphthylamine, etc.) - the titration then runs from 39 to 49 cubic centimeters of nitrite.

There is always a possibility of a loss of nitrous acid in acid solution. This method is based on 109 determinations on 22 different samples in various concentrations of hydrochloric acid, including 34 determinations where the "H" acid was first dissolved in sodium bicarbonate, and no loss of nit-

rous acid could be detected whenever the titration was properly carried out. The diazotization is instantaneous to within a half a cubic centimeter of the end-point when the concentration of hydrochloric acid is from 0.365 to 0.900 normal, figured in the volume at the close of the titration. To avoid loss of nitrous acid which is due to a local concentration of nitrite, whirl the beaker in a rotary motion without lifting it from the bottom of the ice-dish, and run the nitrite in slowly a half cubic centimeter at a time up to 38 or 39 cc. This need take no more than two to three minutes. See that no precipitate remains on the bottom of the beaker, then add two drops of nitrite at a time, testing with KI-starch solution until an instantaneous blue develops which is permanent for two minutes. From a faint-blue to an instantaneous deep-blue is only a matter of two drops nitrite, and the deep-blue end-point is permanent in the cold for almost in indefinite length of time. The titration is accurate to two drops of nitrite -- the titration is complete in ten minutes.

Next in importance to the proper concentration

of hydrochloric acid is the volume of the solution, for in volumes much under 250 cc., the diazonium salt will precipitate out, and there is then danger of a loss of nitrous acid owing to a local concentration of the nitrite. The "H" acid titrates into perfect solution without exception in volume between 250 and 300 cc., of course, providing that no sodium chloride is present. Any precipitate on the bottom of the beaker is easily crushed with a thick glass-rod (3/8" or better) tipped with a piece of rubber tubing (policeman) and titrated into solution. The titration is complete only when no precipitate remains on the bottom of the beaker. Usually no trouble is experienced, but occasionally samples of "H" acid contain small quantities of hard particles sufficient to throw the titration off, and too low. An occasion might arise where the "H" acid would have to be dissolved with sodium bicarbonate.

Finally, the starch solution must be used with care. When the glass-rod from the starch solution is dipped into everything, it is unfit for any subsequent nitrite determination. In that case a blue develops when but one cc. titration or less is

obtained. The fault, then, is with the starch solution. With "H" acid the most delicate end-point is obtained by spreading a large drop of the diazo solution on a spot-plate and dropping a drop of starch solution onto it.

The use of sodium bicarbonate in the determination is unnecessary, and since any small amount of sodium chloride will salt the diazonium compound out of solution, the chances of a loss of nitrous acid are increased.

Equivalent proportions:-

<u>"H" acid</u>	<u>NaHCO</u>	<u>NaNO</u>	<u>HCL</u>
368.218 gr.	84.008 gr.	69.01 gr.	36.468 gr.
2.000	.54624	.37483	.19808

Solutions:-

Sodium nitrite, N/10. Factor 1.07 to 1.09

Dissolve 7.35 grams of CP gran. per liter. Standardize with well purified tolidin (0.5 gram sample,) - the tolidin used was recrystallized from alcohol, and has a melting point of 129 degrees C., and a crystallizing point of 126.5 degrees C.

The weighing of 10 grams of "H" acid, diluting to 500 cc. and titrating a 100 cc aliquot part is used only in approximate work, inasmuch as with a

low acid solution the diazotization is very far from instantaneous, and a sharp end-point is impossible. When sodium bicarbonate is used, sodium chloride will throw the diazonium salt out of solution, increasing, thereby the chances of a loss of nitrous acid. Without bicarbonate the determination is complete only when all precipitate is titrated into solution. With low acidity an especially with bicarbonate there is a tendency to undertitrate; with a poor starch solution there is a tendency to over-titrate.

1 cc. N/10 Na NO₂ \approx .36812 grams "H" acid.

"H" acid Mother Liquor.

100 cc. sample of mother liquor in a 400 cc. beaker. Boil off SO_2 (one hour,) keeping at constant volume with distilled water. Titrate 50 cc. aliquot part with N/5 sodium hydrate.

"H" ACID DIAZO ANALYSIS.

To analyze the "H" acid diazo group, it is necessary to make a Diazobenzol solution of exactly known value. For this purpose we must first have a quantity of C.P. Aniline. The idea of using any old sort of Aniline and to determine its percentage by titration with Nitrite or in any other way is absolutely wrong. Aniline cannot be titrated with Nitrite. The basicity can be determined by titration with an acid but the end-reaction is not sharp, consequently the determination is quite uncertain.

It is very easy to make some Aniline that will answer all the requirements. The commercial Aniline Oil is practically A C.P. material; the chief impurity being a certain amount of moisture. This must be eliminated.

Take a good grade of commercial Aniline Oil (beware of the so-called C.P. Anilines offered by some dealers; they are usually not even quite soluble in acid), one that is completely soluble in diluted Muriatic Acid and distill off a certain part of it untill the

first milky distillate runs quite clear. Then change the condenser and distill off (this time through a perfectly clean condenser) a little more of the Aniline until the new condenser is washed out well by the Aniline vapors. Then change the recipient and catch the Aniline that comes over now, separately, stopping distillation when about 20% of the originally taken quantity remain in the distilling flask. The first milky distillate and the one that did wash out the new condenser is rejected; the same is done with the residue of the distillation. The main part, that has distilled through the washed out condenser, is perfectly dry and practically C.P. Aniline Oil. Fill it in a clean dry flask and close with well fitting cork (not glass and not rubber stoppers.)

The standard Aniline solution can be made up either in Normal strength (93 grams to 1000 cc.) or 100 grams Aniline can be dissolved to one Liter. It makes no difference which is done; only the figuring is different.

All measuring instruments used in the following must be controlled: flasks, cylinders, pipettes, and the actual volumes must be figured on. If many analyses are made, it is best to use always the same instrument for measuring off the same solution. If this is done it is easy to figure out beforehand, and for once and for all, the value of the prospective Diazosolution. I will give a concrete example.

Let us assume that we have weighed, on an analytical balance, in a small beaker or weighing glass, 10,024 grams of our pure redistilled Aniline Oil. 20 cc. of water are added, and then 30 cc. of C.P. Hydrochloric Acid of 1.2 specific gravity. By stirring, a solution results which is brought into a glass stoppered graduated cylinder of 100 cc. capacity. The beaker is carefully rinsed into the cylinder with small portions of water and finally the cylinder is filled up to the 100 cc. mark with water. Let us assume that,



in controlling the cylinder, we have found that it contains, when filled to the 100 cc. mark, 99.8 grams of water of 15 degrees C. that is, 99.8 cc. So we have 10,024 grams Aniline in 99.8 cc. After mixing thoroughly the solution can be filled into a clean, dry bottle. If closed with a cork it will keep for quite a long time. If crude commercial acid has been used for dissolving the Aniline the solution will very quickly turn dark which must not happen.

Of this Aniline solution 10 cc. are brought into a clean 100 cc. cylinder (glass stoppered.) Let us assume that we use again the same cylinder that was used for dissolving the Aniline Oil (of course, after washing it out very thoroughly.) Let us further assume that the pipette we use for measuring off the 10cc. actually holds only 9.93 grams water of 15 degrees C. up to the mark. We have now all the figures we need for figuring the prospective value of the Diazo solution we are going to make.

We weighed 10.024 grams Aniline and brought it to 99.8 cc.

Of this solution we took 9.93 cc. and we are going to diazotize same and to bring the volume to 99.8 cc.

99.8 cc. contain 10.024 grams Aniline; the 9.93 cc. contain X.

The X figures out 0.9974 grams. This quantity we are going to dilute to 99.8 cc. Sol. cc. will contain 0.009994 grams Aniline. As 93 parts Aniline correspond to one molecule (319 parts) of "H" acid, the 0.009994 grams Aniline will correspond to 0.03428 grams of "H" acid. That is: each cc. of the Diazobenzol solution we are going to use for the titration will mean that the tested sample contains 0.03428 grams of "H" acid. As long as the original Aniline solution is used and as long as we use always the same Pipette and the same cylinder this figure will prevail. If a different quantity of Aniline is weighed and brought to 100 cc. (in our case to 99.8 cc.) or of the

instruments are changed the measuring is done with, then the value of the prospective Diazo-solution must be figured out anew.

After bringing the 10cc. of Aniline solution into the 100cc. cylinder, the sample of "H" acid to be tested is first made ready.

The sample is weighed or measured off. Take 1 to 2 grams of dry "H" acid or about 3 grams of a paste; if the "H" acid is in solution take about 5 grams or 5 cc. The "H" acid is distributed in water and dissolved by stirring into the paste obtained 50 cc. of a 10% soda ash solution. If a solution of "H" acid is to tested, attention must be given to the fact that the solution must NOT contain free caustic alkali. If this should be the case, the caustic alkali must be neutralized by adding Muriatic acid and the precipitate formed dissolved with soda ash. The "H" acid solution must be cold (room temperature.) When the "H" acid solution is ready the Aniline is



diazotized. Proceed as follows: To the 10 cc. Aniline solution which is in the 100 cc. cylinder, add so much cold water that the volume is about 50 cc. Then add clean, washed, broken ice until the volume is about 80 cc. or a little more. It takes quite a while to get the ice in through the narrow neck, so the liquid becomes quite cold without any special precautions. Now add a solution of Sodium Nitrite containing about 0.85 grams of pure NaNO_2 . This is an excess, but it is absolutely essential to have an excess as otherwise the Diazotation of the Aniline is not complete. Mix well and then dilute with cold water up to the mark. Shake for a while to insure complete mixing and make sure that all the ice is liquified. After complete liquification continue mixing for a while, then the Diazo-solution is ready for use.

As we need a Diazo-solution for testing, it is best to take out of the cylinder 5 or 10 cc. and place same in a test tube. It is easy to adjust matters with a pipette so that exactly 90 or 95 cc. remain in the cylinder. But remember that in reading the graduation after titrating you have to subtract from 90 to 95 cc. and

not from 100 cc.

Now the "H" acid solution that is to be tested is stirred, and 5 or 10 cc. of the Diazo-solution are run in with a pipette. A deep red color forms that remains in solution if same is rather diluted; if concentrated the color has a great tendency to crystallize. A drop of the solution is brought on filter paper; it will form a red blot that will slowly spread and give a colorless outer rim. Now a drop of the Diazo-solution in the test tube is applied near the red blot. Where the Diazo-solution and the colorless rim touch, a red color forms as long as there is plenty of "H" acid left in the solution. Gradually more Diazo-solution is run into the "H" acid with the pipette, always stirring well while this is being done. When the reaction grows weak in testing the red blot, common salt is given into the color solution which by stirring will dissolve and precipitate the red dye as a dark crystalline mass, leaving the solution very light colored. In this solution the "H" acid can be

detected very easily. The more Diazo is run into the "H" acid the weaker the color forming by testing on filter paper becomes, and the quantities of Diazo added at one time are gradually diminished. First 2 cc., later about 1cc. And towards the end a few drops at a time are added. When the reaction grows so weak that you are not sure whether or not there is really Red forming on the paper, the analysis is finished and the Diazo-solution remaining in the cylinder is read off. In testing toward the end the Diazo-solution must not be applied NEAR the colorless rim of the color mass, but must be drawn THROUGH this colorless rim. The outer parts of a rim is always pure water; a little further inside there is a weak salt solution; it is in the inner part of the colorless rim that contains the last traces of "H" acid and to find these the Diazo-solution must be brought inside of the rim where it will slowly mix with the "H" acid solution.

If we had taken our 5 cc. for testing,

leaving in the cylinder 95 cc. of Diazo-solution and if after the titration the cylinder still contains 63 cc. then we have used 32 cc. for the titration. And the sample of "H" acid analyzed contains 32 times 0.03428, that is (see page 2) 1.097 grams of "H" acid (Molecule 319)

When a man gets used to this work he will work very quickly; he will know from the strength of color reaction on the paper how much more Diazo he may add safely without over-titrating. In this case no extra precautions are required. But if a man is beginning and works slowly then there is danger that the Diazo-solution becomes too warm and is thereby decomposed. In this case the cylinder with the Diazo-solution should not be kept open on the table but should be kept immersed in a pail of ice water. The same is the case if several samples are to be tested. If the Diazo-solution is kept thoroughly cold it can be used for several titrations, but the quickest worker cannot make two or three correct analyses with the same Diazo-solution unless he keeps the solution cold.

This analysis is not only the correct quantitative test for "H" acid, but it is at the same time an excellent qualitative test as it shows impurities present which no other method does. If the "H" acid is pure the color forming on paper is clean red up to the very end. Any impurity will show in the latter stage of the titration by a false color forming, usually a brownish shade. The stronger this brown color and the more Diazo it takes to neutralize this brown-forming matter, the more impure the "H" acid is and the less clean will be the dyes made from same.

Conclusions of the analysis:

Practically pure and absolutely dry Aniline must be used.

The diazotizing must be done ice cold and with a considerable excess of Nitrite and in strongly acid solutions.

The Coupling must be done in a solution made alkaline with Alkali-CARBONATE. Caustic Alkali or Ammonia do not give correct results.

Any deviation from these main principles tends to increase the apparent percentage. If the Aniline is not pure you will have to use more Diazo-solution than you should use, and thereby calculate the percentage of your material too high. If the theoretical quantity or too little Nitrite is used, the Aniline is not all diazotized; this is proven by the fact that colors made in this way are oily and smell of Aniline Oil. As not all of the Aniline is diazotized, you will use again more Diazo-solution than you should and find your percentage too high.

The coupling proceeds smoothly only in a Carbonate solution. Diazo-solutions are rather stable in a solution of Soda Ash. If you over-titrate a Naphthol-Sulphonic acid, that is, if you add more Diazo-solution than corresponds to the Naphthol-Sulphonic acid, you can test on filter paper for Diazo with a drop of Naphthol-Sulphonic acid solution, and you will find that the excess of Diazo added can be found in the color mass several minutes after adding the excess of Diazo.

With caustic alkali this is not the case; the decomposition is then very rapid, a part of the Diazo being transformed into the Iso (Nitroso) compound, while the main part is simply converted into Phenol. That is: you lose a part of your Aniline, thereby requiring more Diazo than you should and you make Phenol which also takes up some Diazo thereby increasing the quantity of Diazo still more.

If Alkali Carbonate is used you have always time to mix the mass perfectly before the Diazo is decomposed; you utilize all the Aniline for the determination of your Sulphonic acid. If you use Caustic Alkali you have not time to mix thoroughly before a part of the Diazo is decomposed. The mixing is also the reason why I prefer to add as much Diazo as possible to the mass while same is liquid and well mixable; if the salt is added from the start or too soon, the mass is rather thick and hard to mix quick enough.

Para-Nitraniline Method for the Analysis of

"H" acid Diazo Group/

Another method for analyzing the diazo group is carried out with the use of N/20 diazo p-nitraniline solution.

Solutions required:-

(a) Nitrosamine solution.

(b) Standard N/20 b-naphthol solution.

Preparation of Nitrosamine.

100 grs. of p-nitraniline are dissolved in 200 cc. of concentrated hydrochloric acid 36% and 100 cc. H_2O . Heat until dissolved and pour it slowly, while stirring, into

50 cc conc. hydrochloric acid CP

350 grs. ice

150 " H_2O

Then add, all at once, 53 grs. 94% $NaNO_2$ (dissolved in the least quantity of water.) Agitate until a clear solution is obtained. Keep at 0-5 degrees C. Then add 1600 cc of cold, "neutral salt" solution. Stir for 2 hours at a temperature of 0-5 degrees C.

The above solution is now poured into a caustic salt solution, at 0. degrees C., very slowly with very good agitation. Do not allow the temperature



to rise above 10 degrees C. Stir 2 hours at 0.10 degrees, allow to stand over night, filter off nitrosamine and wash thoroughly with cold neutral salt solution, 0.5 degrees C.

"Neutral salt" is made by saturating water with NaCl and precipitating the CaO, MgO Al and Fe₂O₃ with N/2 NaOH, excess to Phenolphthalein, filtering and neutralizing with N/3 hydrochloric acid.

Yield about 400 moist $\text{C}_6\text{H}_4\begin{matrix} \text{NO}_2 \\ \text{N:NONa} \end{matrix}$

Determination of Nitrosamine in the Paste.

Weigh 5 grs. of the paste and add 100 cc H₂O and stir until all the lumps are broken up and dissolved. Add 10 cc concentrated hydrochloric acid and stir 2 hours. Filter, wash and make up to 250 cc. Place 25 cc. of N/20 b-naphthol in 800 cc. beaker, add 600 cc. H₂O and neutralize the alkalinity with N/1 acetic acid. The neutral point is reached when the fluorescence disappears, now add 10 grs. of cryst. sodium acetate and 50 grs. of sodium chloride and titrate with the nitrosamine solution until an excess of diazo is shown using a dilute solution of "H" acid on spotting a ring on filter paper.

1cc of N/20 b-naphthol = .0995 grs.





The above caustic salt solution is made by dissolving 500 grs. of NaOH in 1000 gr. of the neutral solution.

Preparation of N/20 b-Naphthol.

Dissolve 7.205 grams of redistilled b-naphthol in 300 cc of water and add 6.5 grams of sodium hydrate CP. Warm until all the b-naphthol is dissolved and make up to 1000 cc. in a volumetric flask.

Preparation of N/20 Diazo p-Nitraniline Solution.

N/20 diazo = 9.95 grams 100% nitrosamine+3 moles
or 5.46 " hydrochloric acid.

An equivalent amount of the nitrosamine corresponding to 9.95 grams are rubbed in a mortar with water and transferred to a 1000 cc. beaker and made up to 700 cc. 12 cc. of concentrated hydrochloric acid are added and stirred for 2 hours, filtered and washed. Make up to 1000 cc. in a volumetric flask.

Standardization of N/20 Diazo Solution.

25 cc. of N/20 b-naphthol are placed in an 800 cc. beaker with 600 cc. distilled water.



N/1 acetic acid is added until the fluorescence just disappears. Add 50 grams of sodium chloride, 10 grams of sodium acetate and titrate with the diazo solution in an ice-water bath, using dilute "H" acid as an indicator until when spotted on filter paper the colorless rim gives permanent color with "H" acid solution.

Analysis of the "H" acid With the Diazo Solution.

Dissolve 10 grams of "H" acid in water and dilute to 250 cc. in a 1000 cc. volumetric flask.

Place 50 aliquot part of "H" acid solution (corresponding to .5 gram sample) in a 400 cc beaker and dilute with 150 cc. of water and 25 cc. of N/1 sodium acetate and 25 cc. N/1 acetic acid. Add 25 grams of sodium chloride and titrate with N/20 diazo-para-nitranilin solution using a dilute solution of "H" acid as an indicator in the ring spot on filter paper.

1 cc. diazo solution \equiv .018406 grams "H" acid.

MISCELLANEOUS DATA.

Report on the Solubility of "H" acid and amino salt in water, HCL and brine.

"H" acid

Solubility in water, expressed in parts of 100%

"H" acid (mol. wt. 368) per 100 parts of water.

Temperature Degrees C	Parts /100
89 degrees	5.34
79 "	4.50
70 "	3.74
58 "	2.87
50 "	2.62
36 "	1.91
30 "	1.60
21 "	1.30
10 "	1.05
5 "	Freezes

Solubility in 20% brine.

86 "	1.00
22 "	0.60

Solubility in acidulated water (1 part 20 degrees Be' HCL in 20 parts water) is very much the same as in water itself.

Solubility in amino salt.

Solubility in water

Solubility in 10% brine

Temperature	Parts/100	Temperature	Parts/100
90 degrees	27.0	92 degrees	14.6
85 "		85 "	
80 "	25.0	80 "	12.0
68 "	21.8	70 "	10.8
62 "	21.1	65 "	6.4
48 "	19.7	38 "	4.0
38 "	14.9	19 "	2.7
21 "	10.7		

Solubility in 20% brine.

Temperature	Parts/100
85 degrees	4.95
75 "	4.78
70 "	4.24
59 "	3.36
50 "	1.82
19 "	0.88

PLANT REPORTS.

In order to keep an accurate account of the operations of the plant, to serve as a check on the several changes that each batch undergoes as it passes through to the final product, operators are supplied with data sheets to be filled out with accurate time statements and measurements of every batch. These reports are checked by the chemist and superintendent each morning and are a condensed account of the plants daily history.

From the daily report sheets the data is entered on monthly report cards. The data supplies all the information necessary to compute plant efficiency and also to provide a means of detecting errors in the operation. For a facsimile of one of the report sheets see blue print on opposite page.

From the several daily reports a condensed daily report is made out and sent to the plant executive office to be filed. These reports provide data from which plant efficiency and costs are computed.

A sample condensed report is shown as follows:

"H" acid Plant Report.

Amino Salt Section.

Sulphonations	Started Nos.	Finished Nos.
Nitrators	" "	" "
Reductions	" "	" "
Saltings	" "	" "
Batches filtered		Batches pressed

Analysis.

Batch No.	Weight	%	100%	Lbs.per	100 lbs.	Naphth.
" "	"	"	"	"	"	"

"H" acid Section.

Fusions	Started Nos.	Finished Nos.
Acidulations	" "	" "
Batches filtered"	"	Batches pressed.

Analysis.

Batch No.	Weight	%	100%	lbs. per	100lbs.	Amino S.
" "	"	"	"	"	"	"

Efficiency to Date.

Amino Salt	"H" acid.
Average for day	Lbs. per 100 lbs. Naphth .Lbs. per
	100# Amino S.

Average to date	
this month	" " " "

Average to date	
last month	" " " "

APPARATUS AND STORAGE TANK CALIBRATION.

Apparatus	Diameter	Length	Specification
Nitration montejus	3ft.8"	5ft	Lead lined
Reduction tanks	7ft.	8ft.	Wood lead lined
Red.Filtrate storage	5½ft.	5½ft.	" " "
Salting tank	9½ft.	6ft.	Wooden
Amino salt montejus	4ft.	6ft.	Lead lined
Fusion storage tank	4ft.	3ft.	Steel cone bottom
Neutralizing tank } Acidifying tank }	5ft.	4ft.	{Steel, lead lined {Cone bottom
Crystallizing tank	5½ft.	5½ft.	Wooden
"H" acid montejus	2 2/3ft.	5ft.	Lead lined
Mixed acid storage	2ft.	3ft.	Steel
18 degree oleum "	2½ft.	2½ft.	Steel
25 " " "	3½ft.	4ft.	{Steel {Cone, bottom.

APPARATUS REQUIRED FOR A PRODUCTION OF
60,000 LBS. OF "H" ACID PER MONTH.

Sulphonators	4
Nitrators	2
Nitration Montejus	2
Reduction tanks	4
Reduction circulating pumps	4
Reduction press	2
Reduction wash water storage tanks	2
Salting or precipitation tanks	4
Amino salt montejus	2
Amino salt filter press	2
Amino salt hydraulis presses	2
Mixed acid tanks (storage)	2
18 degree oleum storage tanks	4
25 " " " "	4
Fusion autoclaves	3
Fusion storage tanks	2
Neutralizing tanks	1
Acidifying tanks	1
Crystallizing tanks	1
"H" acid montejus	1
"H" acid filter presses	2
"H" acid hydraulic presses	2

RAW MATERIAL CONSUMPTION FOR AN "H" ACID
PLANT PRODUCING 47,000 LBS. PER MONTH.

Raw Material	Charge	Consumption per day	Consumption per month.
Naphthalene	375	1 500	45 000
18 Oleum	525	2 100	63 000
25 Oleum	2 625	10 500	315 000
Mixed Acid	483	1 950	60 000
Iron	700	2 800	84 000
Salt	2 520	10 000	300 000
Sodium hydrate	630	3 150	94 500
20 hydrochloric acid	700	9 350	280 000

The above figures represent the Raw Material Consumption for a plant producing 46 950 lbs. of "H" acid per month, an average of 1 565 lbs per day. For this production of "H" acid there is a total production of 2 625 lbs. of 100% amino salt per day.

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Although the afore-discussed process of the manufacture of "H" acid is a representation of my own services as chemist, a few references to work done by German and English chemists should be made, inasmuch as our process is but a development of their efforts.

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